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FATE, TRANSPORT AND TRANSFORMATION OF TOXIC SUBSTANCES: SIGNIFICANCE OF SUSPENDED SEDIMENT AND FLUID MUD

by

Maynard Nichols, Richard Harris and Galen Thompson

Virginia Institute of Marine Science
School of Marine Science
College of William and Mary
Gloucester Point, Virginia 23062

and

Bruce Nelson

University of Virginia
Charlottesville, Virginia

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Project Manager

Duane Wilding

U.S. Environmental Protection Agency
Chesapeake Bay Program
2083 West Street - Suite 5G
Annapolis, Maryland 21401

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Observations of flow, salinity, suspended material, pH, and dissolved oxygen were accomplished in Bay-wide longitudinal sections and at four anchor stations in the northern Bay between March 1979 and April 1980. The observations cover a range of conditions, including seasonal high-low river discharge, sediment influx, neap-spring tide range, and oxygenated-anoxic water. Samples of suspended material, fluid mud, and bed sediment were analyzed for their particle size, organic matter, and metal content.

Metal concentrations of As, Cu, Mn, Ni, Pb, Sn, and Zn in fluid mud and bed sediment per gram of material decrease seaward from a maximum in the Baltimore-Susquehanna River Area. The metals Mn, Pb, and Zn are four to six times greater than Fe-corrected average shale, indicating major human input and significant accumulation in this zone.

Metal concentrations of Cd, Cu, Pb, Ni, and Zn are maximal in surface suspended material from the Central Bay. They are higher than landward near potential sources and they exceed concentrations in bed sediment 2 to 80 times. The enrichment is not natural compared to average shale or plankton; it is most likely created by bio-accumulation.

Transport of particle-associated metals from major sources follows either hydrodynamic pathways leading to particle accumulations by the estuarine circulation, or bio-ecological routes leading to bio-accumulation.

Management and monitoring strategies are provided to reduce potentially toxic metals to acceptable levels and warn management agencies of toxic hazards.

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FOREWORD

Every year a substantial quantity of toxic substances enter the drainage, water and floor of the Chesapeake Bay. The threat of toxic metal contamination lies in the fact that regional production is increasing with an increase in industrial activity and an increase in sewage discharge. Reportedly, thousands of new potentially toxic compounds are developed every year. Although toxic effects and mortalities in the Bay environment have not been demonstrated, disturbing changes have been observed over the past decade, e.g. a decrease in abundance of striped bass and oysters, a lack of shad runs in the upper Bay, the disappearance of grass and declining crab and clam catches. Toxic effects may be subtle and alter the Bay's ecosystem over long time periods. The significance of the problem is evident in widespread and long-term Kepone contamination of the James Estuary. By transfer to all components of the environment and along the food chain, Kepone threatened the health and seafood resources of man. Such accidents and continued threats led to the Toxic Substances Control Act of 1976. To manage toxics and protect the Bay requires an expanded knowledge of concentration levels, transport routes and reservoirs of potential contaminates. This report aims to provide new data on the occurrence and concentration of heavy metals for more effective planning and use of the Bay.

EXECUTIVE SUMMARY

This report aims to provide new information that meets selected objectives of the EPA-States Toxics Plan of Action; i.e. (1) to determine the state of the Bay with respect to the distribution and concentration of selected metals in suspended material and fluid mud; (2) to establish the temporal variations of sediment and metal loading; (3) to identify potential zones of metal accumulation and trace their transport routes, and (4) to provide recommendations for monitoring contaminated sediment.

Field observations provide longitudinal coverage of the Bay with transects into Baltimore Harbor and Hampton Roads. They include contrasting conditions of seasonal high-low river discharge and sediment influx, as well as neap-spring tide range and oxygenated-anoxic water. Suspended material collected on Nuclepore filters, was analyzed by flame AA for Fe, Mn and Zn and by flameless AA for As, Cd, Cu, Hg, Ni, Pb and Sn. Laboratory procedures followed EPA quality control standards using USGS Standards. The survey occupied 122 stations, accomplished 5,576 measurements including 633 analyses of 6 to 11 metals in suspended material and fluid mud.

Physical, chemical and sedimentological conditions for transport and accumulation of toxics in the Bay are variable with time and distance seaward. Bay water is partly-mixed, well-buffered against pH change and well-oxygenated except in summer when near-bottom water of the axial basin is anoxic. Salinity and sediment influx vary seasonally with river discharge and form steep seaward gradients near the inner limit of salty water. Characteristics of suspended material define three broad zones: (1) the turbidity maximum (stations 12-18) with high suspended loads, fine particle size and low organic percentages; (2) the central Bay (stations 8-11) with low suspended loads, coarse particle size and high organic percentages; (3) the near-entrance reaches (stations 1-7) with intermediate suspended loads, moderate particle size and organic percentages. Sediment in deeper parts of the central Bay is fine-grained, moderately organic and depositing relatively fast. These conditions favor accumulation of metals and fluid mud.

Mean concentrations of As, Cd, Cu, Pb, Hg, Ni, Sn and Zn are maximal in surface suspended material from the central Bay. The concentrations are higher than farther landward near major potential sources, the Susquehanna River and Baltimore Harbor. They are also 2 to 80 times greater than maximal concentrations in fluid mud of the northern Bay and Baltimore Harbor. Cd, Cu and Pb of surface and mid-depth water are 3 to 12 times higher in summer than in spring. This trend, together with high percentages of organic matter, suggests bio-accumulation is responsible for the marked central Bay anomalies.

Mean concentrations of As, Cu, Mn, Ni, Pb, Sn and Zn in fluid mud and bed sediment decrease with distance seaward from a maximum in the Patapsco-Susquehanna River area. This accumulation is close to major sources of contamination and it may form by entrapment of suspended material from the Susquehanna in the turbidity maximum.

Concentrations of Cd, Cu and Pb (we./we.) in suspended material vary more than 2-fold over a tidal cycle. These fluctuations are partly associated with tidal variations of current, suspended load, particle size and organic content. Together with seasonal changes in source input and bio-sedimentologic processes, they make Bay metal content highly variable.

Significant correlation coefficients for suspended material are scant. Of note are Mn-Fe, Cu-Zn, and Cu-Pb correlations in the northern Bay. In bed sediments, significant correlations occur between all metals except Hg, but metals generally lack relationships to organic content and particle size.

Metal-Fe ratios of bed sediment decrease with distance seaward from the Susquehanna River indicating the river is a major source of Mn, Ni and Zn. Metal-Fe ratios of suspended material from the northern Bay are similar to those in fluid mud because the material is derived from the mud by repetitive resuspension.

Enrichment factors, derived from metal-Fe ratios normalized to average shale, show Pb and Zn are abnormally high in northern and central Bay bed sediment. They indicate the Susquehanna River is the major anthropogenic source and its impact extends seaward to the Potomac River mouth. Abnormally high factors of Cd, Cu, Ni, Pb and Zn in surface suspended material of the central Bay relate to high organic loads. This enrichment is not natural with respect to either natural shale or plankton; it is most likely created by bio-accumulation of metals from distant sources. Enrichment factors for Cd, Pb and Zn from central Bay suspended material exceed those for Baltimore Harbor and the Rhine Estuary.

Hydrodynamic pathways of particle associated metals from a Susquehanna source follow the estuarine circulation, mainly: (1) seaward through freshwater reaches off the Susquehanna mouth; (2) partial entrapment in the turbidity maximum; (3) partial seaward escape through the upper estuarine layer, particularly along the western shore; (4) landward transport through the lower estuarine layer, particularly along the eastern shore of the lower Bay; and (5) downward settling into sinks of the central and northern Bay. Bio-ecological pathways include: (1) ingestion by benthic filter feeders; (2) uptake by bacteria, phytoplankton, zooplankton and fish; and (3) decomposition and settling of particulate material.

Research is needed to determine the character of bioaccumulation in plankton, the chemical significance of sediment resuspension, the importance of episodic events, the cause of large metal variations and how the tributaries interact with the Bay as a source or sink for metals and sediment.

These findings fill a gap in our knowledge of the Bay where little has been known about metal content in two important reservoirs, fluid mud and suspended material.

ABSTRACT

This research aimed to determine the distribution of selected metals in suspended material and fluid mud, to identify potential zones of toxic accumulation and trace their transport routes.

Observations of flow, salinity, suspended material, pH and dissolved oxygen were accomplished in Bay-wide longitudinal sections and at four anchor stations in the northern Bay between March, 1979 and April, 1980. The observations cover a range of conditions including seasonal high-low river discharge and sediment influx as well as neap-spring tide range and oxygenated-anoxic water. Samples of suspended material, fluid mud and bed sediment were analyzed for their particle size, organic matter, and metal content.

Metal concentrations of As, Cu, Mn, Ni, Pb, Sn and Zn in fluid mud and bed sediment decrease seaward from a maximum in the Patapsco-Susquehanna River area. The metals Mn, Pb and Zn are 4 to 6 times greater than Fe-corrected average shale indicating major human input and good accumulation in this zone.

Metal concentrations of Cd, Cu, Pb, Ni and Zn are maximal in surface suspended material from the central Bay. They are higher than landward near potential sources and they exceed maximal concentrations in bed sediment 2 to 80 times. The enrichment is not natural compared to average shale or plankton; it is most likely created by bio-accumulation of metals from distant sources.

Transport of particle-associated metals from major sources follows either hydrodynamic pathways leading to particle accumulation by the estuarine circulation, or bio-ecological routes leading to bio-accumulation.

Monitoring strategies are provided to reduce potentially toxic metals to acceptable levels and warn management agencies of toxic hazards.

This report is submitted in fulfillment of Grants R806002-01-02 by the Virginia Institute of Marine Science, School of Marine Science, College of William and Mary under sponsorship of the U.S. Environmental Protection Agency. This report covers the period 1 July 1978 - 30 August 1982.

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SECTION 1

INTRODUCTION

Every year about 2 million tons of sediment and a substantial load of trace metals enter Chesapeake Bay (1). The metals are derived from either natural sources or from man's activities. Helz (2) established that at least one-half of the total input of cadmium (Cd), lead (Pb), copper (Cu) and chronium (Cr) to the northern Bay is derived from human sources. However, no single source predominates for all metals. The most important human source is sewage and industrial wastes (3). Additionally, metals are supplied by harbor activities including shipping, spills and disposal of dredged material, by fallout of atmospheric material enriched in Pb and zinc (Zn), and by mining and industrial activities in the watershed. Metal content of suspended sediment from the Susquehanna River reportedly is higher than most U.S. East and Gulf coast rivers (4).

The threat of toxic metal contamination lies in the fact that regional production is believed to be increasing with an increase in industrial activity and with an increase in sewage treatment plants (5). Reportedly, thousands of new potentially toxic compounds are developed every year (5). Although trace metals are required in low concentrations to maintain a healthy biota, they can be toxic if present in excess concentrations. The tragic accidents caused by mercury (Hg) and cadmium (Cd) poisoning in Japan, like Kepone in the James River, amplify the fact that contamination extends to seafood resources leading to man. Examples of specific toxic effects or mortality of Chesapeake biota to individual metals are lacking, but disturbing changes have been observed over the past decade (3). Among the changes are: a decrease in abundance striped bass and oysters, a lack of shad runs in the upper Bay, the virtual disappearance of rooted aquatic plants, and declining crab and clam catches. Toxic effects may be subtle and alter the Bay's ecosystem over long time periods (6).

Until now, the information needed to assess the impact of metals on the Bay is scant. Data for predicting "hot spots" and monitoring toxic metals are inadequate. In particular, the distribution and metal content of suspended material and fluid mud is poorly known.

This report aims to provide new information that meets selected objectives of the EPA-States Toxics Plan of Action (6):

1.) To determine the existing distribution and concentration of selected metals in suspended material and fluid mud of the Bay.

2.) To establish the magnitude of temporal variation associated with tidal flow, freshwater discharge and sediment loading, and other processes.

3.) To identify major zones of metal accumulation in suspensions and trace their sedimentological transport routes.

4.) To provide recommendations for monitoring of contaminated sediment.

This report provides a data base describing the state of the Bay relative to the content of selected metals in suspended material and fluid mud. It touches on processes of accumulation and transport that can produce the observed distributions. Implications are drawn but major management questions are addressed in a companion management of the Chesapeake Bay Program.

Suspended material and metals are studied together because metals are adsorbed, bound and precipitated on suspended material (8). They can be picked up by filter-feeding organisms or metabolized by plankton and reach high concentrations. Once metals are tied up in suspended form, they behave like natural sediment. They are subject to transport by waves and currents from their source or sites of erosion to their sink or sites of deposition. As suspended material settles, it transfers metals from the water to the bed and can remove metals from dynamic segments of the Bay. Generally, the residence time for metals in suspended form is much longer than in dissolved form. In brief, suspended material deserves attention because it can play a major role in the transport and accumulation of potentially toxic metals.

The term "fluid mud" describes dense suspensions of sediment with concentrations of 10 to 480 g/l equivalent to densities of 1.005 to 1.30 g/cm^3. The mud can be generated either naturally, e.g. by storm wave agitation of the bed, floods and strong currents, or artifically, e.g. by dredging, disposal or propellor wash on the bed. Commonly, it is derived from less dense suspensions that settled from the water to the bed. Therefore, fluid mud is an intermediate stage between mobile suspended material and the quasi-static mud that settles and consolidates to form a permanent bed.

Fluid mud is chemically important because it contains a higher metal content, expressed in weight per volume, than suspended material by virtue of its high concentrations (> 10 g/l). Because the mud accumulates as loose watery masses near the bed, it can create a high vertical gradient of suspended concentrations and associated metals. When the mud becomes anaerobic, this chemical gradient is enhanced by pH and Eh changes and the potential flux between mud and overlying water can become great. In summary, fluid mud deserves attention because it serves both as a reservoir for potentially toxic metals and as a medium for chemical transfer.

Prior data on the occurrence of metals in suspended material of the Bay is scant. Carpenter, et al. (9) revealed marked variability of metals discharged by the Susquehanna River into Chesapeake Bay. Carpenter, et al. (9) suggested that the metal content of fine suspended sediment in the northern Bay forms a longitudinal gradient. They revealed marked temporal variations of metals discharged from the Susquehanna River. Analysis of weekly samples for 18 months in 1965-1966 showed the river is enriched in iron (Fe), manganese (Mn), zinc (Zn), copper (Cu) and nickel (Ni) during short periods in winter (9). Monthly sampling at 3 stations in the northern Bay during 1971 (9), showed that fluctuations of particulate Zn may be affected by inflow as well as by biogenic cycling. From observations of Fe and Zn, Eaton, et al. (10) showed that Susquehanna sediment extends 60 to 80 km downstream in surface water. Loss of particulate Fe was attributed to particle coagulation rather than mixing and dilution (10). The sources, dynamic behavior and Bay-wide distribution of suspended material is partly known from studies of Schubel (17) and Biggs (12).

SECTION 2

CONCLUSIONS

The main findings of this study are:

1.) Hydrographic observations indicate Bay water is partly-mixed, well-buffered against pH change and oxygenated, except in summer when near-bottom water of the central Bay below 10 m depth is nearly anoxic. Physical and chemical conditions for transport and accumulation of toxics are highly variable with time, depth and distance seaward from the Susquehanna River.

2.) Mean concentrations of As, Cu, Mn, Ni, Pb, Sn and Zn in fluid mud and bed sediment decrease with distance seaward from a maximum in the Patapsco-Susquehanna River zone. This zone of accumulation, the turbidity maximum, is close to major sources of contamination and it may entrap contaminated river-borne suspended sediment from the Susquehanna.

3.) Concentrations of Cd, Cu, Pb, Ni and Zn are maximal in surface suspended material from the central Bay. Enrichment is not natural compared to average shale and plankton. It is associated with a high organic percentage and most likely is created by bio-accumulation of metals from distant sources.

4.) Transport of particle-associated metals from the Susquehanna follows both hydrodynamic pathways leading to particle accumulation by the estuarine circulation, or bio-ecological routes leading to bio-accumulation.

5.) Research is needed to determine: the character of bio-accumulation in plankton, the chemical significance of sediment resuspension, the importance of episodic events, the cause of wide metal variations, how the tributaries interact with the Bay as a source or sink for metals and sediment.

6.) These findings fill a gap in our knowledge of the Bay where little has been known about metal content in two important reservoirs, fluid mud and suspended material.

SECTION 3

RECOMMENDATIONS

1.) The state of the Bay should be improved with respect to water quality by reducing source input of potentially toxic metals, Cd, Cu, Ni, Pb, and Zn from Bay-wide wastewater and industrial discharges. Additionally, the turbidity, or suspended solids load, which contains more than 60 percent organic matter in the central Bay, should be alleviated by reducing input of nutrients that stimulate organic production. The turbidity maximum can be reduced by any means that will stabilize the bed and deter entrapment of river-borne sediment. Entrapment may be reduced by regulating inflows during periods of high sediment influx and by enhancing salt mixing in the zone of the maximum.

2.) Develop and implement a monitoring system for the Bay and its tributaries that will warn management agencies of encroaching toxic hazards.

3.) Institute further research to determine: (1) the rate, route, seasonality, and amount of bioaccumulation in plankton; (2) the chemical significance of repetitive sediment resuspensions; (3) the importance of episodic events in release of metals from bed sediment; (4) why metal content varies over a wide range; (5) how the tributaries interact with the Bay as a source or sink for metals and sediments; (6) the effects of future changes in metal-sediment transport routes and rates through numerical and hydrodynamic modeling.

TYPING GUIDE SHEET

SECTION 4

METHODS AND PROCEDURES

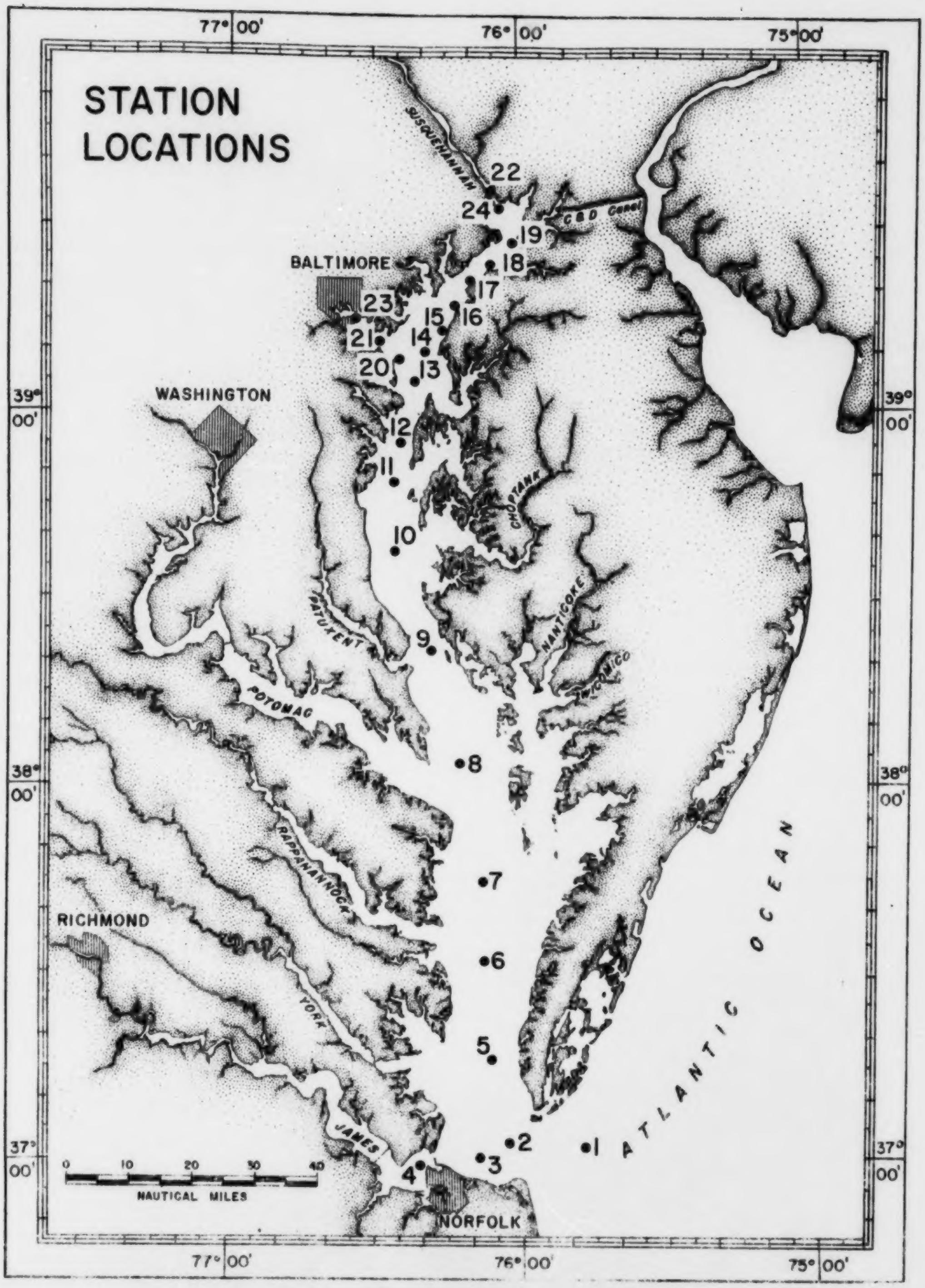
SAMPLING LOCATIONS AND APPROACH

In the absence of definitive data on metal content of suspended material and fluid mud, sampling stations were located to provide general coverage of the Bay axis from the Susquehanna River entrance to the ocean. A greater density of stations was established across the turbidity maximum of the northern Bay where gradients of salinity and suspended material are greater than elsewhere. Stations were also established seaward of potential contamination sources at Baltimore Harbor and Hampton Roads.

Observations were planned to cover two annual cycles of water and sediment discharge including contrasting high and low river inflow, i.e. between March, 1979 and September, 1979. Several cruise observations were planned to meet contrasting conditions of spring and neap tide range, i.e. August 6-12 and August 28-30, 1979. All observations and sampling were scheduled close to slack water (± 1 hour) to permit comparison of data from station to station without the effects of sediment resuspension from the bed. Generally, two to five stations were occupied during each slack water for a total of 18 to 23 stations along the Bay axis (Fig. 1). On each cruise the same stations were occupied and they were positioned by shipboard radar, or Loran C fixes, on charted bouys or landmarks.

Our approach to sampling and selection of observational parameters followed three lines: (1) to collect suspended material for analysis of toxic metals, (2) to characterize the water in which the metals occur, i.e. the water quality and chemical regime, (3) to characterize the sediments with which the metals associate.

The selected metals include those that are: (1) potentially toxic and accessible, including As, Cd, Cu, Hg, Ni, Sn, and Zn (13); (2) poisonous having created toxic crises elsewhere, including Cd, Cu, Hg, and Pb (13); (3) enriched in Chesapeake bed sediments including Cd, Cu, Pb, and Ni (2, 14); (4) relatively widespread and potentially useful as surrogates for geochemical analysis including Mn and Fe. Water quality and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YORK
JAMES
CHOPTANK
NANTICOKE
WICOMICO
ATLANTIC OCEAN
1
2
3
4
5
6
7
8
9
10
11
12
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14
15
16
17
18
19
20
21
22
23
24
0
10
20
30
40
NAUTICAL MILES

Figure 1. Location of stations occupied for hydrographic observations and sediment sampling.

chemical parameters were selected to include commonly measured parameters used to define water quality and water masses in estuaries including temperature, salinity, dissolved oxygen, pH and total suspended material (solids). Additionally, the suspended concentration provides a means to express metal concentrations per weight of dry sediment. Attention focused on particle size and organic (carbon) content because metal content often varies with these parameters (13). Water content of bed sediment defines the concentration of dense suspensions and in turn the sediment density and thickness of fluid mud.

FIELD OBSERVATIONS

We sampled the water by hydrographic casts using either a 2-liter plastic van Dorn bottle or a vacuum pump with polyethylene tubing. To sample near-bottom water, the water bottle was deployed in a tripod frame set at 30 cm above the bed. In the water column, we sampled at standard depth intervals: i.e. (1) for total water depths greater than 12 m, at the surface, 8 m below the surface, 3 m and 1 m above the bed; (2) for water depths less than 12 m, at the surface, 6 m below the surface, 2 m and 1 m above the bed. Water depths were determined either with a standard meter wheel or a differential Bell and Howell pressure transducer, type 4-351 zeroed at the surface. Additionally, the hydrographic casts included *in situ* measurements of temperature and dissolved oxygen using probes of a Yellow-Springs meter, model 54ARC, calibrated according to standard practice specified by the manufacturer.

We obtained bed sediment and fluid mud with either a stainless steel Smith-MacIntyre grab or a Bouma box core. To avoid metal contamination, the units were coated with plastic Gulvit compound and we obtained subsamples from inner parts of the grabs or boxes. Additionally, we fitted the box core with a special acrylic liner, Lukin and Nichols (47), to prevent metal contamination and to retain a portion of relatively undisturbed sediment for X-ray radiography in the laboratory. Once retrieved on deck, a plastic spatula was used to remove the top 2-3 cm of sediment, and sub-portions from various depth intervals. Subportions were stored frozen in plastic bags for metal analysis and in tarred aluminum containers for water content determination. The rim of each container lid was sealed with plastic tape to deter evaporation.

LABORATORY PROCEDURES

Water and Sediment Analyses

After recovery of water samples on deck, we measured aliquots of water for pH using an Orion model 399A meter. The unit was calibrated according to the manufacturer's instructions and standardized at each station with two buffers, pH 4.0 and

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TYPING GUIDE SHEET

pH 7.0. Additionally, salinity was determined in the laboratory on a Beckman RS-7A salinometer calibrated according to the manufacturer's procedures. For total suspended solids, we followed procedures of Strickland and Parsons (15) which utilize 0.45μ Millipore membrane filters after leaching of soluble material and tarring in a dehumidified room. Water samples were vacuum filtered fresh, within 3 hours after recovery. The filters were stored frozen and reweighed after drying at 85°C for 12 hours. The 0.45μ pore size is an accepted cutoff size for differentiating dissolved and particulate substances (16).

Water content of bed sediments and fluid mud was determined gravimetrically be weight loss. Approximately 20 ml of sample, which was stored in tarred aluminum containers, was oven-dried at 105°C for 24 hours and reweighed after cooling to room temperature in a dehumidified room. The weight loss was taken as the weight of water in the sample and the percent water content was calculated according to the equation:

$$\omega_c = \frac{\omega_w}{\omega_s} \times 100$$

Water content, ω_c , is the ratio in percent of the weight of water in a given sediment mass, ω_w , to the weight of the oven-dried solid particles, ω_s. Bulk density of the sediment, defined as the weight per unit volume of the total sediment mass, was derived from the water content data assuming a grain density of 2.7 using the relation:

$$\rho = \frac{2.7\ \omega_t}{\omega_d + \omega_w\ 2.7}$$

where ω_t is the total wet sediment weight, ω_d is the dry sediment weight and ω_w is the weight of water (48).

Organic content of bed and suspended sediment was determined gravimetrically by weight loss after combustion. For suspended sediment the Millipore filters used for determination of total concentration were combusted in a tarred ceramic crucible at 385°C for 8 hours. After cooling in a dehumidified room to ambient temperature, the remaining ash was reweighed. For control, empty crucibles were processed with the sample crucibles including cleaning, drying, weighing, combustion and reweighing. The analysis gives an estimate of the organic content based on percent of total dry weight.

Particle size of suspended material was analysed in a Coulter Counter, Model TAII. Samples were run in two ways: (1) fresh, immediately after recovery, mainly with a 140μ tube, and (2) after storage in a refrigerator and dispersion in Calgon and ultrasonic treatment (1 min.) using Coulter Counter tubes of 30 and 140μ aperture diameters (equivalent to volume-size diameters of 0.6-12μ and 2.8-56μ. This technique permitted distinguishing size differences between samples run fresh and dispersed in a common tube. The differences give an indication of the degree of particle aggregation. Resulting size data were compiled into cumulative curves from which the statistical parameters, mean, median and standard deviation were derived.

Metal Analyses

For trace metal analysis of suspended material, we initially vacuum-filtered a measured volume of fresh Bay water temporarily stored in carboy reservoirs, through a preweighed 0.45μ pore size, 47 mm diameter Nuclepore membrane filter until they clogged. The filters were prefiltered with methanol to open air-clogged pores. After filtering sediment, each filter was rinsed with distilled and de-ionized water to remove sea salts. Filters were then transferred with teflon coated tweezers to plastic petri dishes, and kept at less than 0°C for transport and additional analysis.

Suspended matter collected on Nuclepore filters was digested with concentrated HNO_3 and HCl (17), with the final volume adjusted to 50 ml volumetrically. By this means we determined "suspended metal concentrations". Stock solutions were prepared according to EPA Standards (17) with calibration standards made up in HCl to match sample acid concentrations. Fluid mud, dried at 65°C, was similarly digested (0.25 g) and prepared for analysis.

Flame atomic absorption was used to determine Fe, Mn, and Zn. Graphite furnace (flameless) atomic absorption was used to obtain concentrations of As, Cd, Cu, Hg, Ni, Pb and Sn. Parameters and conditions for these analyses are shown in Table 1. Background correction, with either a hydrogen or deuterium lamp, was always applied.

An indication of the need for standard addition analyses was obtained by measuring the recovery of known metal additions to digested suspended sediment and fluid mud samples. This method revealed the matrix suppression of the absorption signals. Recoveries were > 93% for all metals except Hg in suspended sediment and Hg, Pb in fluid mud, which required standard addition corrections.

Quality Control of Metal Analysis

The following precautions were routinely observed in an effort to keep metal contamination from various sources as low as possible: (1) Acids were distilled at sub-boiling temperatures in a fused silica still (Quartz Products Corporation, Plainfield, N.J.). (2) Water was softened and passed through 25 µm filters and reverse osmosis membranes prior to sub-boiling distillation. (3) All reagents and water were quantitatively analyzed for the metals of interest by flameless atomic absorption. (4) Labware was leached in 1:1 (v/v) HNO_3 and thoroughly rinsed with high purity water. (5) Procedural blank levels were continuously monitored for low metal levels during each atomic absorption run.

TABLE 1 PARAMETERS AND CONDITIONS FOR ATOMIC ABSORPTION ANALYSIS

Flame AA - Varian AA5

Specifications	Fe	Mn	Zn
wavelength, nm	248.3, 373.7	279.5	213.9
lamp current, ma	5	5	5
slit, µ	50	50	100
air flow, meter units	7	7	8
C_2H_2 flow, meter units	2	2	2

Flameless AA - Perkin Elmer 703, HGA 2200

Specifications	As[1]	Cd	Cu	Hg[2]	Ni	Pb	Sn
wavelength, nm	193.7	228.8	324.7	253.7	232.0	283.3	286.3
slit width, nm	0.7	0.7	0.7	0.7	0.2	0.7	0.7
lamp current, ma	18	4	10	6	20	10	30
N_2 gas flow	stop 3	norm 3	norm 3	stop 3	norm 3	stop 3	stop 3
sample size, µl	20	20	20	50	50	20	50
dry T, °C	105	105	105	105	105	105	105
dry t, sec	20	20	20	35	35	20	35
char T, °C	1100	300	500	200	500	500	800
char t, sec	15	10	10	15	15	10	15
atomize T, °C	2700	2000	2100(mp)	2300	2700	2700	2200(mp)
atomize t, sec	8	8	8	8(ramp)	8	8	8
signal mode	peak	peak	peak	peak	peak	peak	peak

(mp=max power)

[1] one ml sample + 10 µl 1000 ppm Ni $(NO_3)_2$

[2] one ml sample + 20 µl 50% H_2O_2 + 50 µl conc. HCl (34, 35)

SECTION 5

SCIENTIFIC RESULTS

DATA ACQUIRED

The new data inventory consists of hydrographic and sedimentologic measurements and observations acquired from eight cruises. Table 2 summarizes the data acquired. Altogether the field observations resulted in 122 stations occupied and 5,576 measurements. In the laboratory, 560 samples of suspended material and 73 samples of fluid mud or bed sediment were analyzed for 6 to 11 different metals. These observations and analyses provide a larger volume of data than acquired by previous studies. The data are provided to the EPA Chesapeake Bay Program on computer tape, as computerized printouts and in special scientific reports (20)(21)(22).

PHYSICAL, CHEMICAL AND SEDIMENTOLOGICAL CONDITIONS

River Discharge and Suspended Sediment Influx

The discharge rate of the Susquehanna River at Conowingo between January, 1979 and April, 1980 varied from a daily average peak on March 7, 1979 of 12,544 m^3/s to a minimum on November 3, 1979 of 25 m^3/s (23). Figure 2A shows the variations of discharge prior to, and during, the observation period. Corresponding sediment concentrations (Fig. 2B) range 470 mg/l to 13 mg/l equivalent to about 278,000 and 2,190 tons/day. The Susquehanna contributes about 50 percent of the total freshwater input to the Bay (22). Observations of the first Bay-wide cruise and the time series were made two to four weeks after periods of peak inflow and sediment influx.

Temperature

The longitudinal distribution of temperature in March-April, 1979, cruise 1, varied from 10.8°C in near-surface river water to 1.8°C in deeper parts of the central Bay (20). The 5.0°C isotherm, which defines the boundary of the cold bottom water, extends across the central basin from station 7 to 13 at the 6 to 8 m depth. The cool pool represents residual winter-formed water that is incompletely mixed and warmed. Stability of the water is strengthened by freshened near-surface salinity. In

TABLE 2. SUMMARY OF DATA INVENTORY FOR WATER COLUMN MEASUREMENTS.

					PARAMETERS[4]						
Cruise Number	Cruise Date	Type of Observations	Tide[1] Range	Stations[2] Occupied	Temp./Salin.	D.O.	pH	Solids/Metals	Organic Content	Particle Size	Current
1	Mar. 27-Apr. 4, '79	Bay Longitudinal & Harbor Transects	spring	2-21	87/90	84		95/59	59		
2	May 2-10, '79	Bay Longitudinal & Harbor Transects	neap	1-6 8-10 11-21	55/96	53	80	96/38	87		
3	Aug. 6-15, '79	Bay Longitudinal & Harbor Transects	spring	2-10 12-14 17-22	65/75	67	60	71/59	69		
4	Aug. 28-30, '79	Bay Longitudinal & Harbor Transects	neap	1-14 16-21 23-24	70/103	103		73/73	73	36	
5	Apr. 28, '80	Bay Longitudinal Transect	mean	11, 13-14, 16-18, 22	38/38	13	15	34/22	33	22	
6	May 1-2, '80	Bay Longitudinal Transect	spring	13-19, 22	50/50		36	36/24	36	34	
9 (CBI)	June 4-6, '79	Bay Longitudinal Transect	neap	23[3]	210/210	131	182	117/94		94	
T	Apr. 29-May 2, '79	Time series	spring	11, 15, 17, 19	235/220	192	216	266/191	265	254	242

[1] Predicted.

[2] By station number.

[3] Total number of stations.

[4] Total number of measurements.

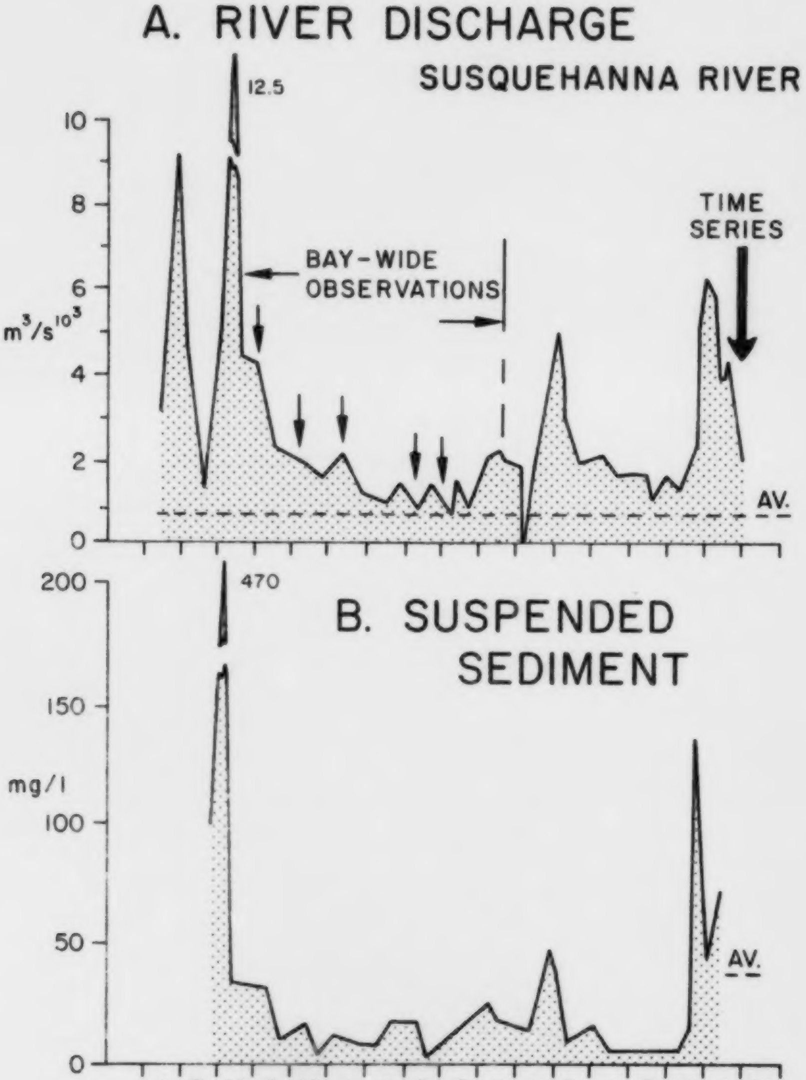


Figure 2. Temporal variations of: (A) Susquehanna River inflow at Conowingo in relation to annual average (983 m^3/s) and observation periods; (B) sediment concentrations during the discharge period. Data from U.S.G.S. (23).

contrast to spring distributions, the summer distributions are isothermal. Temperature measured August 28-30 varied less than 5°C from the Susquehanna River to the ocean, and less than 2°C from the surface to the bottom in deeper parts (20)(21). The temperature distributions are similar to those presented by Stroup and Lynn (25) and Seitz (26) for comparable seasons. Temperature affects oxygen solubility, water density and viscosity which in turn, affects settling rates of suspended material.

Salinity profiles during the observation period were characteristic of a partly-mixed estuary. Salinity increases with depth at all stations (Fig. 3A). Greatest change occurs at 10 to 15 m depth where the vertical gradient reaches 5 ‰ salinity per 2 m. This feature defines a halocline that represents a boundary between a freshened upper layer and a salty lower layer (24). As shown in Figure 3A, mean salinity ranges from nearly fresh (1 ‰) near the river entrance to more than 30 ‰ off the Bay entrance. The transition from fresh to salty water is gradual; however, slight longitudinal gradients form near the 1-5 ‰ and the 25-30 ‰ isohalines. The inner gradient is more pronounced (5 ‰ per 12 km) during high river inflow, e.g. March-April, 1979 than during low inflow, e.g. August 28-30, 1979 (20)(21). With subsiding river inflow from April 1-2, 1979 to August 27-30, 1979, the 5% surface isohaline moved landward 42 km and the vertical gradient weakened. The range of salinity values, patterns and vertical structure are similar to those reported by Stroup and Lynn (25) and Seitz (26) for comparable times of the year.

Dissolved Oxygen

During spring, March 27-April 2, 1979, dissolved oxygen concentrations varied within narrow limits (8.1 to 12.9 ppm). By May, at higher water temperatures, concentrations values were lower, less than 5 ppm, especially in near-bottom water below 12 m. By early June 4-6, oxygen content was nearly depleted in the axial basin below the 8-12 m depth (21). Such a change is an annual event in the Bay (24). It is mainly caused by increased oxygen utilization as temperature increases seasonally. It can be intensified by die-off of plankton and by freshening of near-surface water which increases haline stratification and thereby decreases vertical mixing.

The pH or hydrogen ion concentration, varies within narrow limits throughout most of the Bay. Most values range from 7.2 to 8.3 pH with relatively low values (< 7.5 pH) in the northern Bay between stations 12 and 18 and high values (7.5-8.3 pH) in the Southern Bay. Measurements from the June 4-6 cruise in the middle Bay reveal a decrease in pH values with depth, from

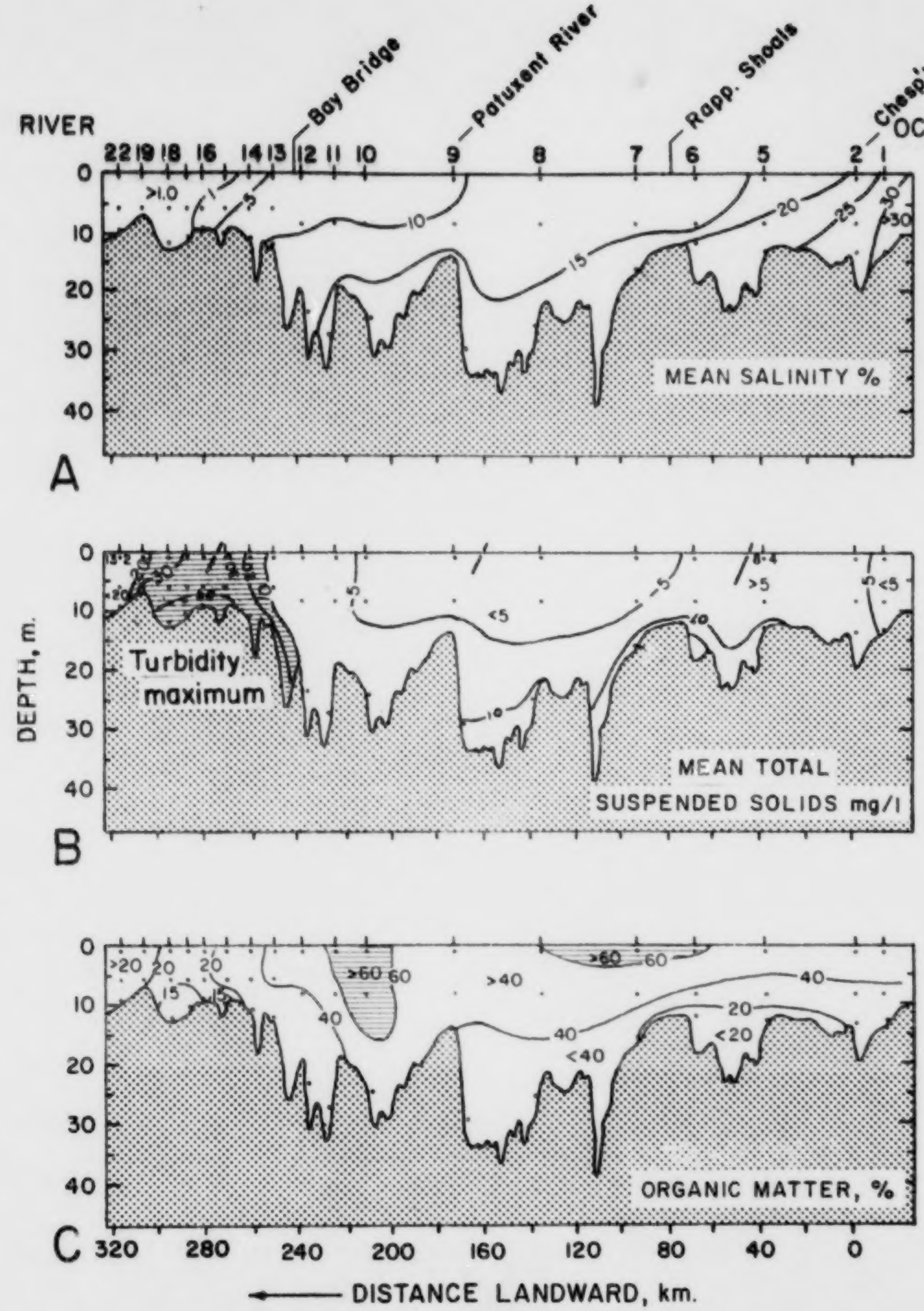


Figure 3. Longitudinal distribution of: (A) mean salinity, upper; (B) mean total suspended solids, middle; (C) mean percent organic matter, lower. Means from all available slack water cruise observations.

8.2 pH at the surface to 7.5 pH at 32 m depth. The range and magnitude of pH is comparable to previous values recorded by Stroup and Lynn (63) and by Seitz (71).

Suspended Material (solids)

The concentrations of total suspended material, which include both organic and inorganic constituents, exhibit three major distributional features (Fig. 3B): (1) a zone of intermediate values, 5 to 9 mg/l, near the Bay entrance between stations 2 and 6. This is a zone where sediment resuspension from the bed. (2) a downward increase with high concentrations just above the bed. Such a vertical gradient in instantaneous profiles can be produced both by downward settling and by resuspension of bed sediment. (3) a zone of relatively high values, greater than 30 mg/l near the inner limit of salty water at 1^{o}/oo salinity, stations 15 to 18. This zone is called the turbidity maximum (11). Concentrations in the maximum (Fig. 3B) are higher than farther seaward in the Bay or landward in river water. With time the concentrations are higher in March-April, 1979, i.e. over 150 mg/l, a time of high Susquehanna inflow and sediment influx, than in August 6-11 at similar conditions of tide, when they were less than 90 mg/l. When longitudinal sections of suspended material obtained at contrasting spring and neap tide conditions are compared, e.g. August 6-11 and August 27-30, it is evident that concentrations in the maximum are 1.5 to more than 2 times greater during spring than during neap tide range. This trend suggests that resuspension from the bed plays an important role in supplying the turbidity maximum.

The mean organic content of suspended material ranges from less than 15 percent by weight in the turbidity maximum to more than 60 percent in near-surface water of the southern Bay (stations 6 to 8)(Fig. 3C). The low percentages most likely form because the total suspended material is "diluted" by inorganic material from the bed. The high near-surface percentages are most likely supported by plankton and their products plus organic detritus (27). Near-surface percentages throughout the Bay are higher in August, 1979, e.g. up to 86 percent, than in March-April, 1979, e.g. up to 47 percent. Relatively low values in near-bottom water of the turbidity maximum persist in measurements from May through August, 1979 (20)(21).

Particle size by volume of non-dispersed suspended material from August, cruise 4, is finest (3.2µ mean) in the zone of the turbidity maximum (stations 12-17) and coarsest (15.5µ mean) in the mid-Bay (stations 8-10). Farther seaward the mean size gradually diminishes to 5.6µ in the ocean. With depth at slack water, mean size varies within narrow limits, largely less than 0.20µ. However, over a tidal cycle at one fixed station and depth, e.g. station 17 at 4 m above the bed, mean size varies from 8.1µ near slack water to 14.0µ near maximum current.

Therefore, the particles are a mixture of relatively fine material that resides in suspension for a long time, and coarse material that is intermittently resuspended from the bed. Mean particle size of slack water samples analyzed dispersed is as much as 8μ finer than non-dispersed material. Greatest change occurs in the turbidity maximum near the 0.5 ‰ isohaline (Fig. 4). This suggests a portion of the suspended material consists of agglomerates. These particles can be created by organic fecal pelletization or by electrochemical cohesive forces (28) or chemical precipitation. When mean size values of dispersed samples from the northern Bay, August, 1979, are compared with samples from the same area, April, 1980, the April samples are coarser by a factor of 2 or more. Also, in near-surface water they exhibit a seaward decrease in mean size from station 19 to 13. The coarse values occur when input of river-borne sediment is relatively high.

In summary, the physical, chemical and sedimentological conditions for transport and accumulation of toxics in Chesapeake Bay are variable with time and distance seaward. Bay water is partly-mixed, well buffered against pH change and oxygenated except in summer when near-bottom water of the axial basin is anoxic. Salinity and sediment influx vary seasonally with river discharge and form steep seaward gradients near the inner limit of salty water. Characteristics of suspended material define three broad zones: (1) the turbidity maximum (stations 12-18) with high suspended loads, fine particle size and low organic percentages; (2) the central Bay (stations 8-11) with low suspended loads, coarse particle size and high organic percentages; (3) the near-entrance reaches (stations 1-7) with intermediate suspended loads, moderate particle size and organic percentages.

Bed Sediment Properties

The Bay is floored by an admixture of sediments from varied sources, the river, shores, sea and organic production in the Bay itself. Despite varied sources the sediment properties change systematically along the Bay axis. As shown in Figure 5A, water content (wet weight) of the top 1 cm of sediment mainly increases from 181% to 440% with distance away from the Susquehanna River mouth (stations 11-16). Except for a slight reduction at station 16 to 18, this trend of water content is accompanied by decreasing bulk density (Fig. 5B), increasing rate of fill (Fig. 5D) and increasing thickness of fluid mud (Fig. 5A). That is, the depth of the density at 1.3 g/cc, equivalent to 480 g/l, increases seaward as the surficial water content increases. In the central Bay basin (stations 8-11), water content is more than 300% and fluid mud exceeds the penetration depth of the box core (44 cm) at most stations. Rate of fill is higher than elsewhere. Farther seaward in partly sandy sediment (stations 1-7) and shoaler depths, the water content diminishes to less than 70%, the bulk density increases to 1.91 g/cc and rate of fill is

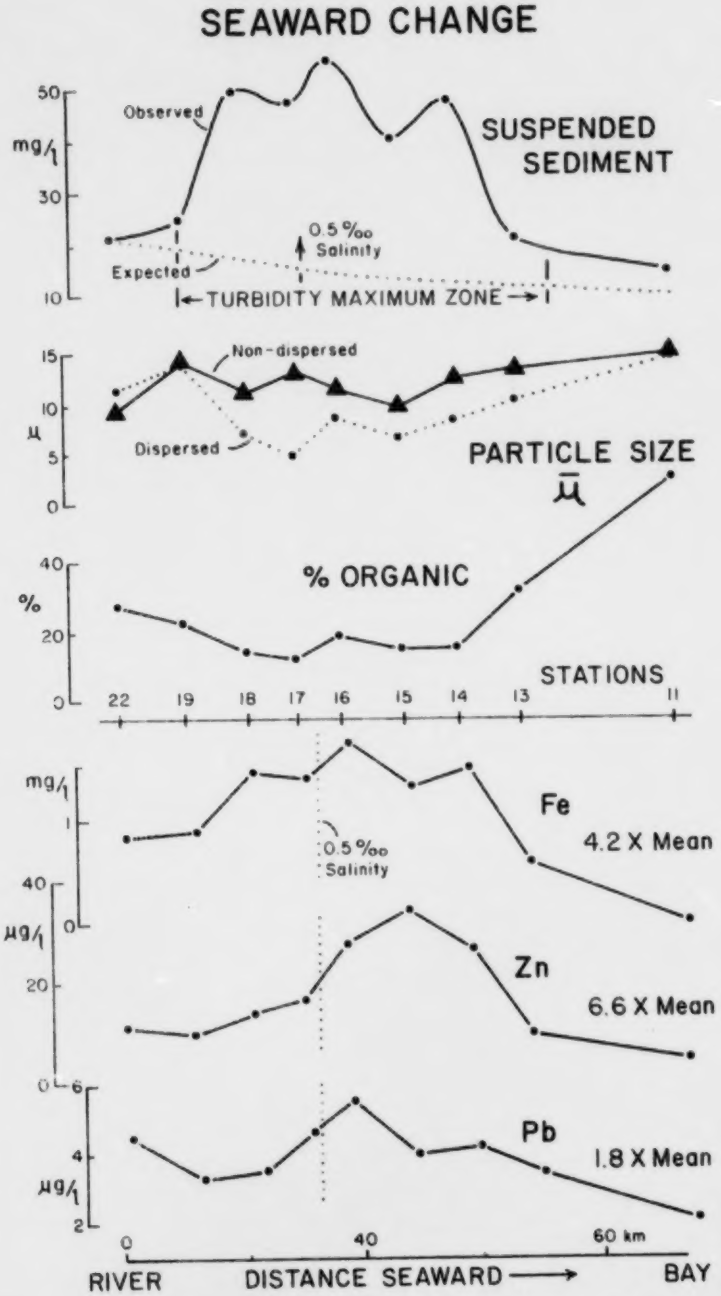


Figure 4. Longitudinal distribution of near-bottom suspended material between stations 11 and 19, northern Bay; total suspended material, particle size, percent organic material.

SEAWARD CHANGE OF SEDIMENT PROPERTIES

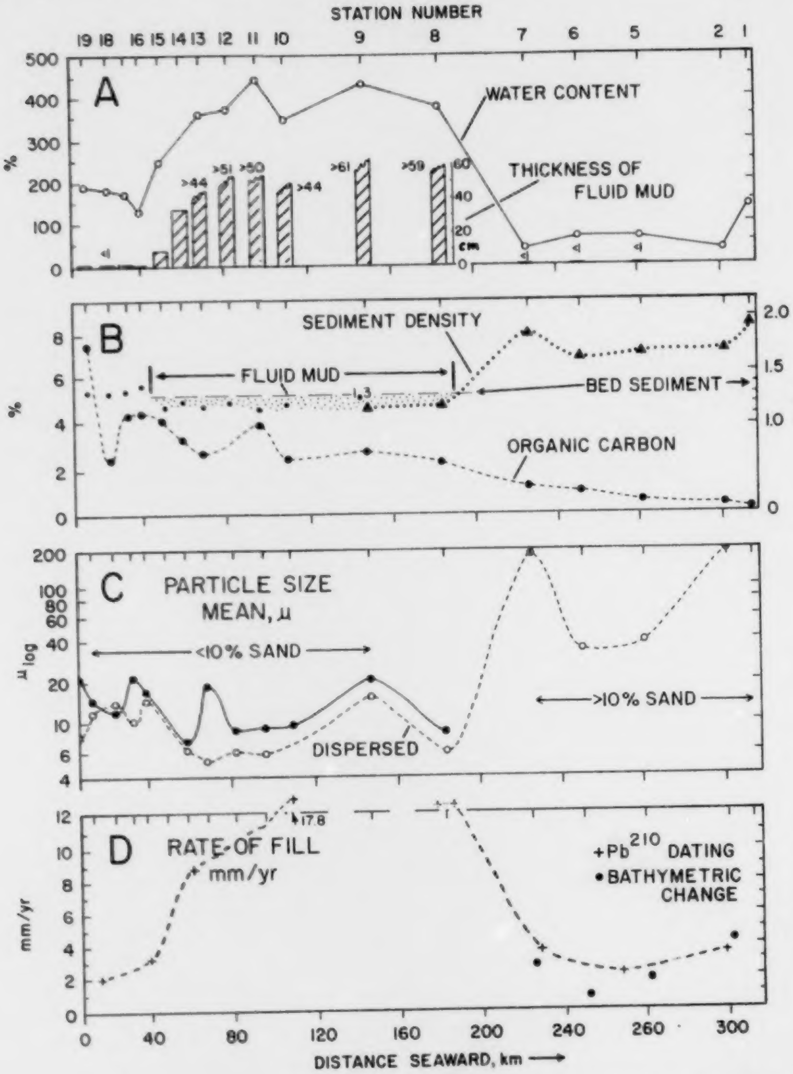


Figure 5. Seaward change in bed sediment properties at stations along the Bay axis from the Susquehanna River mouth (station 19) to the ocean (station 1). Data based on an average of 2 to 6 measurements of surficial sediment for each station. A. Percent water content and thickness of fluid mud. B. Percent organic carbon content and sediment density, zone of fluid mud less than 1.3 g/cc, shaded. C. Mean particle size of non-dispersed samples, solid, and dispersed samples, dashed. D. Rate of fill from different data of associated projects, PB^{210} from Setlock, et al. (30) bathymetric changes from Caron (31).

relatively low. In summary, sediment properties in deeper parts of the central Bay are favorable for accumulation of metals and fluid mud. The sediment is fine-grained, organic carbon percentage is higher than in the Southern Bay and the rate of fill is greater than elsewhere.

HEAVY METAL DISTRIBUTIONS

Suspended Material

The longitudinal Bay-wide distributions of metal concentrations in this section are expressed either as dry weight per gram of suspended material (e.g. μg/g), or as weight per liter of Bay water (e.g. mg/l). The latter units reflect both the metal content and the concentration of suspended material. All metal concentrations are derived from analysis of bulk samples, unfractionated for particle size. However, the mean particle size of suspended material is relatively small, less than 16μ. The distributions are presented in graphs, Figures 6 and 7 displaying median values and ranges for all available data at each station. Additionally, longitudinal-depth sections of mean values for all available data are provided in Appendix 6. Mean and median values reported as "less than" were derived by halving the less than values and incorporating them with averages for regular values. Graphs of longitudinal-depth distributions for each cruise and each metal are given in special reports (20)(21)(22). The distinctive features of the distributions for each metal are given below.

Arsenic--

This metal varies within relatively narrow limits, from 5.85 to 62 μg/g. Locally a few hot spots of high values occur in the central Bay at the surface or at mid-depth, stations 6-9, but many values seaward of station 13 are necessarily reported as "less than". Arsenic in surface suspended material from the central and lower Bay is generally higher than near-bottom suspended material.

Cadmium--

Of the 11 metals analyzed, cadmium is the most variable. It ranges 0.12-790 μg/g with hot spots at different depths between stations 9 and 14 and at station 2. A secondary surface maximum at station 12 reflects potential sources released from Baltimore Harbor or resuspended from old dredged material on the Bay floor. Median values of surface cadmium are distinctly higher in the central Bay than elsewhere except for station one (Fig. 6). The central zone has a higher percentage of organic matter than elsewhere.

METALS IN SUSPENDED MATERIAL
SURFACE

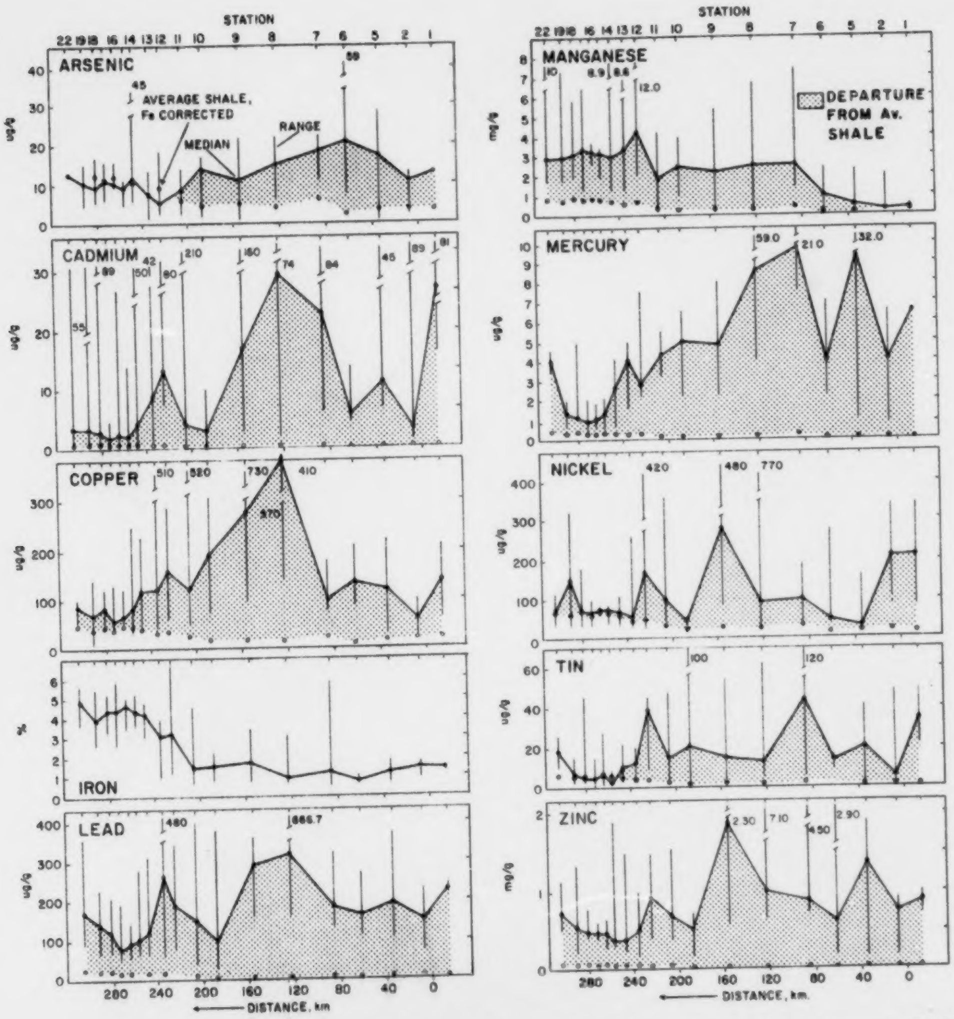
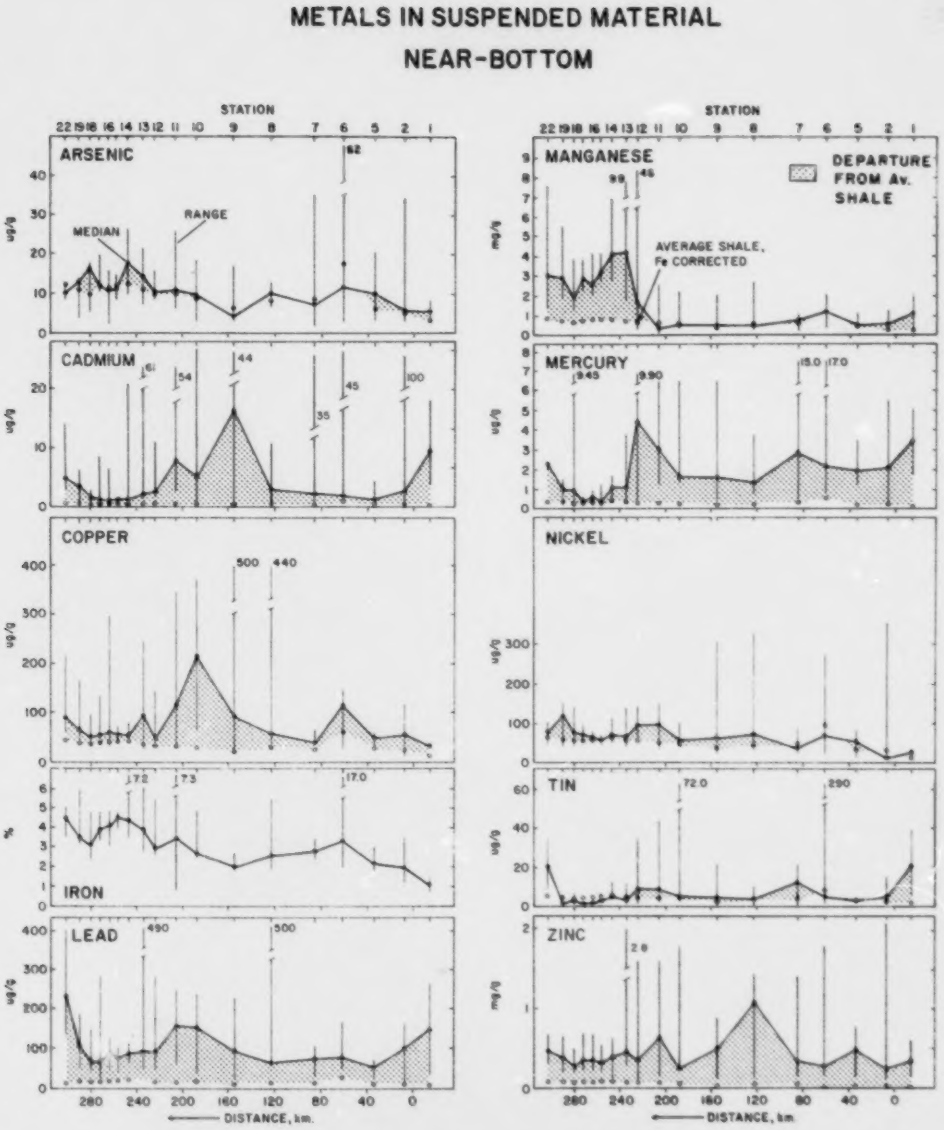


Figure 6. Distribution of metal content in surface suspended material with distance along the Bay axis. Median values and range of concentrations from all available observations of this project. Shaded zone indicates magnitude of departure between median values and mean values for Fe-corrected average shale, open circles.



METALS IN SUSPENDED MATERIAL

NEAR-BOTTOM

Figure 7. Distribution of metal content in near-bottom suspended material with distance along the Bay axis. Median values and range of concentrations from all available observations of this project. Shaded zone indicates magnitude of departure between median values and mean values for Fe-corrected average shale, open circles.

Copper--

The trend for copper resembles the trend for cadmium. It reaches a maximum of 410 μg/g (median value) in surface suspended material of the central Bay, station 8. This is higher than farther landward or seaward. The copper maximum occurs at the same stations as the cadmium and lead maxima. Surface and mid-depth values from the central Bay are higher than near-bottom values by a factor of 2 or more. Stratification is common to most longitudinal copper distributions except in early June (cruise 9) and late August (cruise 4). There is a moderate gradient of decreasing concentrations with distance away from the Susquehanna River mouth, stations 22 to 17. Copper concentrations in the central Bay are 6 to 10 times greater in early August (cruise 3) than in March-April (cruise 1).

Iron--

This metal varies within narrow limits. The extreme range is 0.29 to 17.0%; however, most values are within the range 2 to 5% and the mean is 3.11%. As shown in Figures 6 and 7, iron generally decreases with distance seaward from the river. The greatest reduction in surface suspended material takes place at station 11. With depth, however, iron distributions are relatively constant.

Lead--

This element exhibits a maximum of 320 μg/g (median value) in surface suspended material at station 8. Like cadmium a secondary maximum occurs at stations 12-13 off Baltimore Harbor. There is also an increase toward the Susquehanna River mouth, especially in near-bottom suspended material, which reaches a maximum of 190 μg/g at station 22. Lead ranges from 21 to 730 μg/g with local hot spots greater than 600 μg/g at the surface and mid-depths of the central Bay. Most anomalies occur in the June 4-6 (cruise 9) observations.

Manganese--

This element decreases irregularly from the northern to the lower Bay. It reaches a peak of 4.20 mg/g (median value) at station 12. The greatest seaward change takes place in near-bottom suspended material between stations 13 and 11, where median values drop from 4.20 to 0.31 mg/g (Fig. 7). In June 4-6 and August 6-11, 1979 observations, manganese in the central Bay is lower in the near-bottom water than in surface and mid-depth water by factors of 5 to 50 (21). At this time near-bottom water is depleted in dissolved oxygen (21). By contrast, vertical distributions of manganese in March-April, 1979 are relatively uniform and concentrations are reduced to less than 4.8 mg/g.

Mercury--

This metal ranges 0.05-59 µg/g and reaches a maximum (median) concentration of 9.75 µg/g in surface suspended material of the central Bay, station 7 (Fig. 6). Although near-bottom concentrations are lower and less variable than surface concentrations, a median peak of 4.55 µg/g occurs at station 12 (Fig. 7). Mean surface concentrations of the central Bay are 4 times higher than near-bottom concentrations. The large number of less than values in individual observations precludes distinct longitudinal and temporal trends.

Nickel--

The trend for nickel in surface suspended material resembles lead and zinc. Median values reach a maximum of 280 µg/g at station 9 and a secondary maximum of 170 µg/g at station 12 (Fig. 6). Surface values are more than 2 times higher than near-bottom values and mean vertical distributions are stratified in the central Bay. Except for an anomaly of high values, greater than 400 µg/g, at mid-depth between stations 10 and 12 in June, 1979 (21), temporal changes from cruise to cruise are relatively small.

Tin--

This element exhibits two maxima in surface suspended material, stations 7 and 12 with median concentrations of 44 and 39 µg/g, respectively. This metal exhibits a large range of values, 0.25 to 290.0 µg/g. Mean surface values are generally 2 to 3 times greater than near-bottom values in the central Bay, a trend resulting in vertically stratified distributions.

Zinc--

This metal is very abundant throughout the Bay. Concentrations reach a median peak of 1.90 mg/g in surface suspended material of the central Bay (Fig. 6). Secondary maxima occur at stations 5 and 12. Similar trends are found in near-bottom suspended material, but the peaks are flatter and the median values are about half of those at the surface (Fig. 7). Values range 0.10 to 7.10 µg/g. Local hot spots occur in the central Bay at mid-depth in June 4-6, 1979 distributions, near the bottom in August 28-30, 1979 and at the surface in March-April, 1979 (20)(21). In most distributions zinc is lower in the turbidity maximum zone than elsewhere. Zinc is generally higher throughout the Bay in March-April, 1979 than at other times observed.

When the metal distributions, reported as weight per volume, e.g. µg/l, are examined, it is evident the metal concentrations vary with the distribution of total suspended material. That is, where the suspended concentrations are high, most metal concentrations are also high. For example, in the zone of the turbidity maximum, concentrations of As, Fe, Mn, Ni, Sn and Zn reach a prominent maxima (Fig. 4, Appendix 8). Figure 8A shows a linear trend of iron with total suspended material despite a change of water types from the Susquehanna River through the turbidity maximum and partly saline reaches of northern Chesapeake Bay. By contrast, metals like Cd, As, and Hg with wide ranges and anomalous hot spots, locally depart from the trend. Then too, near-bottom manganese from the central Bay in summer is lower than expected from its concentration of suspended material. Figure 8B shows how zinc, from near-bottom samples in river water, the turbidity maximum and partly saline water of the northern Bay, departs from the linear trend of iron.

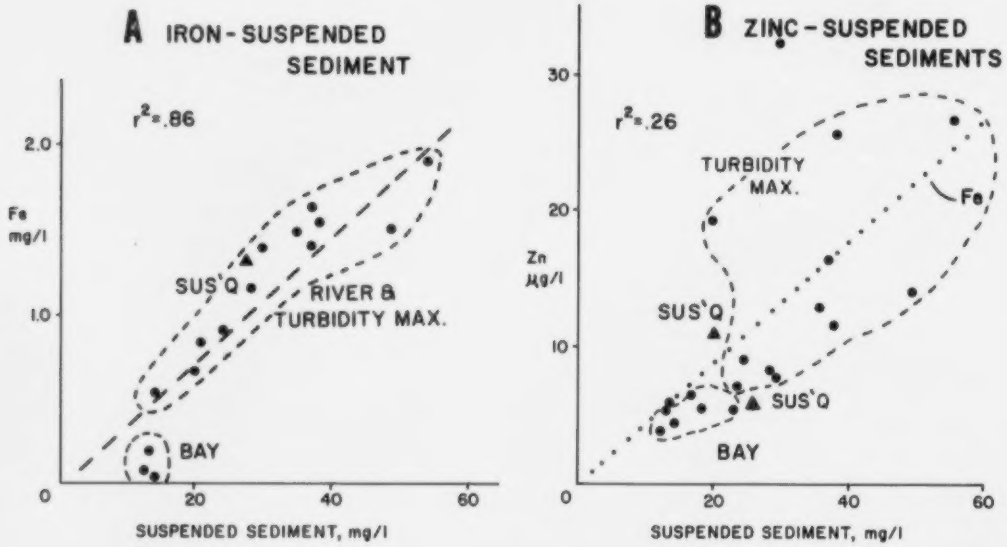


Figure 8. Variation of metal content with total suspended sediment material through a range of conditions from Susquehanna River water through the turbidity maximum zone and partly saline reaches of the northern Bay: A. Iron; B. Zinc; dotted line shows the trend of iron for comparison. Data from near-bottom samples of cruises 5 and 6, April-May, 1980.

In summary, the longitudinal distributions of mean and median metal content by weight are marked by relatively high values of As, Cd, Cu, Pb, Hg, Ni, Sn and Zn in surface suspended material of the central Bay, stations 5-9. Metal concentrations in this zone are higher than farther landward or seaward. Mean surface and mid-depth concentrations are higher than near-bottom concentrations resulting in vertically stratified distributions. Secondary maxima occur at Bay stations 12 and 13 off Baltimore Harbor for surface concentrations of Cd, Mn, Ni, Pb, Sn and Zn, and for near-bottom concentrations of Cu, Hg, Mn, Pb and Zn. Concentrations of Hg, Pb, Zn and to a lesser degree As, Cu and Sn decrease with distance away from the Susquehanna River mouth, stations 22-16. Seasonal changes are marked by a 10-fold increase in surface copper concentrations in summer, May-August relative to March-April. Lead is higher in June observations than at other times whereas zinc is higher in March-April than in early August observations.

Table 3 summarizes the mean metal concentrations and range of values throughout the Bay for all available data of this project.

TABLE 3. SUMMARY OF MEAN METAL CONCENTRATIONS AND RANGE OF BAY-WIDE VALUES IN SUSPENDED MATERIAL: EXPRESSED WEIGHT PER WEIGHT, LEFT; WEIGHT PER VOLUME, RIGHT.

Metal	Mean	Range	Metal	Mean	Range
As µg/g	13.00	0.55-100.00	As µg/l	0.32	0.006-5.00
Cd µg/g	14.16	0.12-790.00	Cd µg/l	0.14	0.003-3.80
Cu µg/g	127.96	9.90-570.00	Cu µg/l	1.84	0.068-17.00
Fe %	3.11	0.29-17.00	Fe mg/l	0.88	0.01-12.00
Pb µg/g	160.30	21.00-730.00	Pb µg/l	2.27	0.10-15.00
Mn mg/g	2.88	0.08-46.00	Mn µg/l	65.13	0.48-1000.00
Hg µg/g	3.89	0.05-59.00	Hg µg/l	0.035	0.01-0.47
Ni µg/g	95.80	4.80-770.00	Ni µg/l	2.00	0.03-34.00
Sn µg/g	17.97	0.25-290.00	Sn µg/l	0.20	0.01-4.80
Zn mg/g	0.75	0.10-7.10	Zn µg/l	11.02	0.55-94.00

Fluid Mud and Bed Sediments

The longitudinal Bay-wide distributions of mean metal concentrations in fluid mud and bed sediment along the axis of Chesapeake Bay are illustrated graphically in Appendix 7. The data were obtained from bulk, unfractionated samples. Distinctive features of the distributions are given below.

Arsenic, Lead, Tin, Zinc--

These metals exhibit similar distributions consisting of maximum concentrations at stations 13-16. Landward toward the Susquehanna mouth, mean concentrations drop irregularly to less than 25 percent of their maximum value. Seaward concentrations decrease irregularly in a broad gradient to the ocean. The maximal values lie off potential metal sources, Baltimore Harbor and Gunpowder River. Station 13 lies near the Kent Island dredged material disposal area, and a zone of high clay content (33).

Copper, Nickel--

These metals exhibit similar Bay-wide trends. Copper reaches a maximum of 44.5 µg/g (mean) at station 19. It remains relatively high, above 25 µg/g, seaward to station 11. Potential human sources of copper are Baltimore Harbor, Kent Island disposal area and the Susquehanna River (2). In fluid mud of the central Bay basin, mean copper values are nearly constant at 17 µg/g but concentrations drop farther seaward in sandy sediment of the lower Bay (Fig. 5C).

Cadmium--

The distribution of cadmium is irregular and values have a wide range. There are three peak concentrations at stations 8, 11 and 15, but the Susquehanna mouth and near-ocean sediment are low.

Iron--

Iron varies within narrow limits. Concentrations are slightly higher at stations 12-15 off Baltimore Harbor, a potential human source. However, iron is an abundant element common to natural sediments.

Mercury--

Since most concentrations of this metal are reported as less than values, distinct trends are not evident in the distributions.

Manganese--

This element exhibits elevated concentrations between stations 13 and 19 with a maximum of 3.9 mg/g (mean) at station 14, seaward concentrations drop rapidly at station 12 and remain low to the ocean except for station 6.

Table 4 summarizes the mean metal concentration and range of values in fluid mud and bed sediment throughout the Bay.

TABLE 4. SUMMARY OF MEAN METAL CONCENTRATIONS AND RANGE OF BAY-WIDE VALUES IN FLUID MUD AND BED SEDIMENT EXPRESSED AS DRY WEIGHT PER WEIGHT.

Metal	Mean	Range
As, µg/g	3.90	0.67-11.00
Cd, µg/g	0.33	0.02-1.40
Cu, µg/g	19.60	0.40-50.00
Fe, %	2.40	0.45-4.10
Pb µg/g	32.00	2.80-99.00
Mn, mg/g	1.30	0.05-6.10
Ni, µg/g	28.50	1.90-64.00
Sn, µg/g	0.52	0.05-2.10
Zn, mg/g	0.15	0.02-0.71

In summary, most Bay-wide metal distributions in fluid mud and bed sediment, except Cd, Fe and Hg, generally decrease seaward from a maximum in the Baltimore-Susquehanna mouth zone, stations 13-19, a potential source of major contamination. Alternately, the seaward decrease is produced by mixing of metal impoverished sediment derived from shore erosion of the central and lower Bay. Moreover, low metal concentrations in the lower Bay are from a zone of coarse-grained sediment.

Harbor Distributions

The distribution of mean metal concentrations in Hampton Roads and Baltimore Harbor is presented in Tables 5 and 6. The stations are located in transects at 5 to 10 mile intervals extending from the central Harbor seaward to, and partly including, the Bay-wide longitudinal section (Fig. 1).

When metal distributions in suspended material and fluid mud from Hampton Roads are compared along transects, the metals Fe, Mn, and Zn exhibit little change (Table 5). However, fluid mud and bed sediment from Hampton Roads (station 4) has higher concentrations of Cu, Pb, Zn, Hg and As than farther seaward, stations 1-3. In particular, copper concentrations in the harbor exceed those in the ocean sediments by more than eight times. Similar gradient are found for near-bottom suspended material. By contrast, surface suspended material from the lower Bay and ocean has higher concentrations of As, Cd, Cu, Pb, Sn and Ni than the Roads. Concentrations in the Bay exceed those in the harbor by 2 to 3 times but they are less than the elevated concentrations in the central Bay.

Fluid mud and bed sediment from Baltimore Harbor (stations 20-21) has higher concentrations of Cu, Hg, Pb and Ni than stations in the adjacent Bay (12 and 13), Table 6. In particular, copper concentrations in the harbor exceed thosein the Bay by 5-fold. Arsenic, however, is more than 5 times greater in the Bay than in the harbor. Similarly, Cd, Ni, Hg and Mn in near-bottom suspended material of the Bay exceed those of the harbor by more than 2 times. In surface suspended material relatively steep gradients form whereby Sn, Ni, Hg and Pb are higher in the Bay than in the harbor (Table 6). Thus, the distributions are complicated and gradients shift for different metals and different depths.

Comparison of harbor values, Tables 5 and 6, indicates bed sediment concentrations from Baltimore are 3 times higher for Fe, 9 times for Mn, 5 times for Ni and 14 times higher for Cu, than Hampton Roads. Near-bottom suspended material from Baltimore is 4 times higher in As and Cu than Hampton Roads. On the other hand, cadmium and mercury are generally higher in suspended material from Hampton Roads than from Baltimore.

TIDAL TIME SERIES

Dynamic Features

Observations over a 13-hour tidal cycle at four anchor stations in the northern Bay, define short-term hydrodynamic and sedimentologic fluctuations affecting temporal variations of metal concentrations. The most prominent feature of the time series is the large fluctuation of total suspended material. For example, as the tidal current increases after slack water, either flood or ebb, the suspended material increases and either flood or ebb, the suspended material increases and reaches a peak just after maximum current (Figs. 9 & 10A). Concentrations increase mainly when the current reaches about 20 to 30 cm per sec. Therefore, the concentration increase lags the increase of current by about one to two hours. Similarly, peak concentrations lag peak current velocity. Subsequently, as

TABLE 5. MEAN METAL CONCENTRATIONS FOR STATIONS IN HAMPTON ROADS AND VICINITY; EXPRESSED WEIGHT PER WEIGHT. FOR STATION LOCATIONS, SEE FIGURE 1.

	Station			
Metal	4 Harbor	3 Bay	2 Bay	1 Ocean
Arsenic, µg/g				
surface	5.4	12.7	7.6	12.7
bottom	15.5	12.8	10.7	5.9
bed	3.0	2.9	1.5	1.5
Cadmium, µg/g				
surface	8.2	144.7	21.3	49.0
bottom	4.1	2.1	23.2	11.4
bed	0.06	0.15	0.03	0.03
Copper, µg/g				
surface	57.0	62.7	62.7	132.5
bottom	80.5	292.0	59.4	36.0
bed	8.4	3.8	1.0	0.65
Iron, %				
surface	3.1	3.3	1.4	0.3
bottom	4.9	2.9	2.1	1.2
bed	1.5	1.3	0.6	0.7
Lead, µg/g				
surface	98.5	131.5	146.0	225.0
bottom	132.2	53.7	95.8	149.5
bed	15.2	9.1	3.7	5.1
Manganese, mg/g				
surface	1.0	1.2	0.6	0.4
bottom	1.8	1.1	0.7	1.1
bed	0.3	0.3	0.1	0.1
Mercury, µg/g				
surface	2.9	2.9	3.7	6.5
bottom	3.9	1.3	2.1	3.3
bed	0.07	0.03	0.03	0.04
Nickel, µg/g				
surface	62.6	71.5	38.5	210.5
bottom	108.2	70.2	121.5	24.5
bed	9.0	8.4	2.8	3.2
Tin, µg/g				
surface	10.0	9.9	15.4	34.8
bottom	10.9	15.6	5.9	22.0
bed	0.5	0.3	0.2	0.1
Zinc, mg/g				
surface	0.9	1.0	0.7	0.9
bottom	0.8	0.8	0.7	0.4
bed	0.07	0.05	0.02	0.02

TABLE 6. MEAN METAL CONCENTRATIONS FOR STATIONS IN BALTIMORE HARBOR AND ITS ENTRANCE REACHES IN CHESAPEAKE BAY, EXPRESSED WEIGHT PER WEIGHT. FOR STATION LOCATIONS, SEE FIGURE 1.

	STATION				
Metal	23* Harbor	21 Harbor	20 Entrance	13 Bay	12 Bay
Arsenic, µg/g					
surface	13.0	16.4	8.8	7.4	7.8
bottom	63.0	21.6	25.5	15.9	11.1
bed	1.1	4.0	3.9	5.3	5.8
Cadmium, µg/g					
surface	<5.5	17.8	8.6	11.4	27.3
bottom	<6.3	2.9	1.0	11.4	5.2
bed	0.5	0.4	0.5	0.4	0.4
Copper, µg/g					
surface	110.0	111.5	86.0	162.6	158.0
bottom	320.0	47.5	60.3	104.1	83.8
bed	120.0	44.5	45.0	26.5	27.8
Iron, %					
surface	1.9			3.0	3.4
bottom	5.4	4.3	3.9	4.0	3.5
bed	4.8	4.9	3.6	3.2	3.3
Lead, µg/g					
surface	87.0	185.0	119.5	267.2	208.6
bottom	240.0	60.5	60.7	162.0	122.1
bed	62.0	164.0	65.5	59.8	48.0
Manganese, mg/g					
surface	4.6	7.0	4.5	3.5	5.1
bottom	3.3	5.8	9.9	4.7	10.5
bed	1.0	2.8	3.2	3.0	1.2
Mercury, µg/g					
surface	1.7	2.8	2.0	3.5	3.6
bottom	1.7	0.4	0.4	1.4	4.9
bed	0.05	0.12	0.03	0.04	0.04
Nickel, µg/g					
surface	28.0	70.2	57.5	103.4	174.9
bottom	49.0	61.8	87.0	86.2	94.0
bed	46.0	49.5	37.2	50.8	28.2
Tin, µg/g					
surface	8.7	17.4	9.2	11.9	33.9
bottom	37.0	10.6	18.8	5.7	12.0
bed	1.8	1.8	1.6	1.2	0.5
Zinc, mg/g					
surface	0.6	1.0	0.7	0.6	0.9
bottom	0.8	0.3	0.5	0.8	0.6
bed	0.3	0.4	0.3	0.2	0.2

*Values for cruise 4, August 28-30 only.

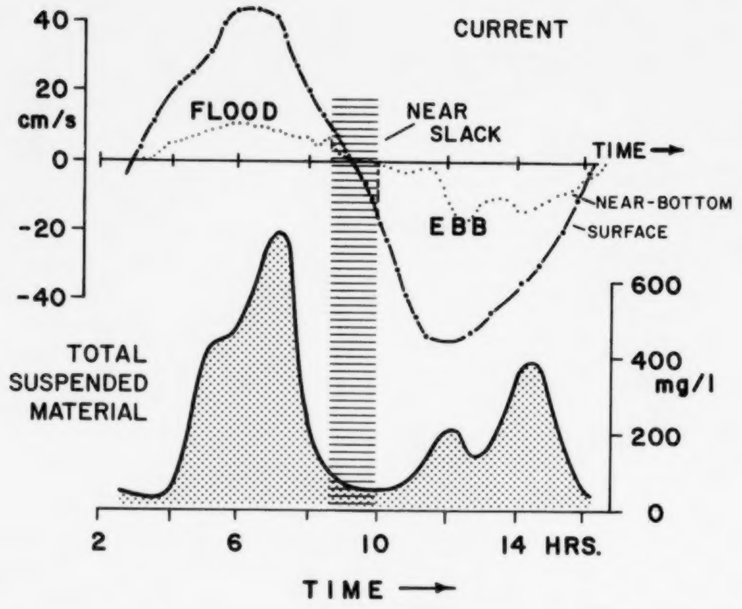


Figure 9. Temporal variation of current velocity and total suspended material at 30 cm above the bed, anchor station 17, April 30, 1980.

current diminishes, suspended material drops to a minimum near slack water. Over an entire cycle, suspended concentrations repeat a cyclic pattern that go up and down with the strength of the current as material is alternatively resuspended and settled to the bed.

The temporal fluctuations of suspended concentrations are greater near the bed than near the surface (Fig. 10). Consequently, the bed is the likely source of suspended material. By contrast, near-surface loads representing a background load remain in suspension for a long time.

The fluctuations of suspended load are accompanied by fluctuations of particle size and organic content. For example, at 30 cm above the bed, station 17, mean size increased from about 11μ near slack water to 15μ near maximum current while corresponding surface size ranged 7.5 to 10.5μ. The background load, which remains in the water column at slack water, consists

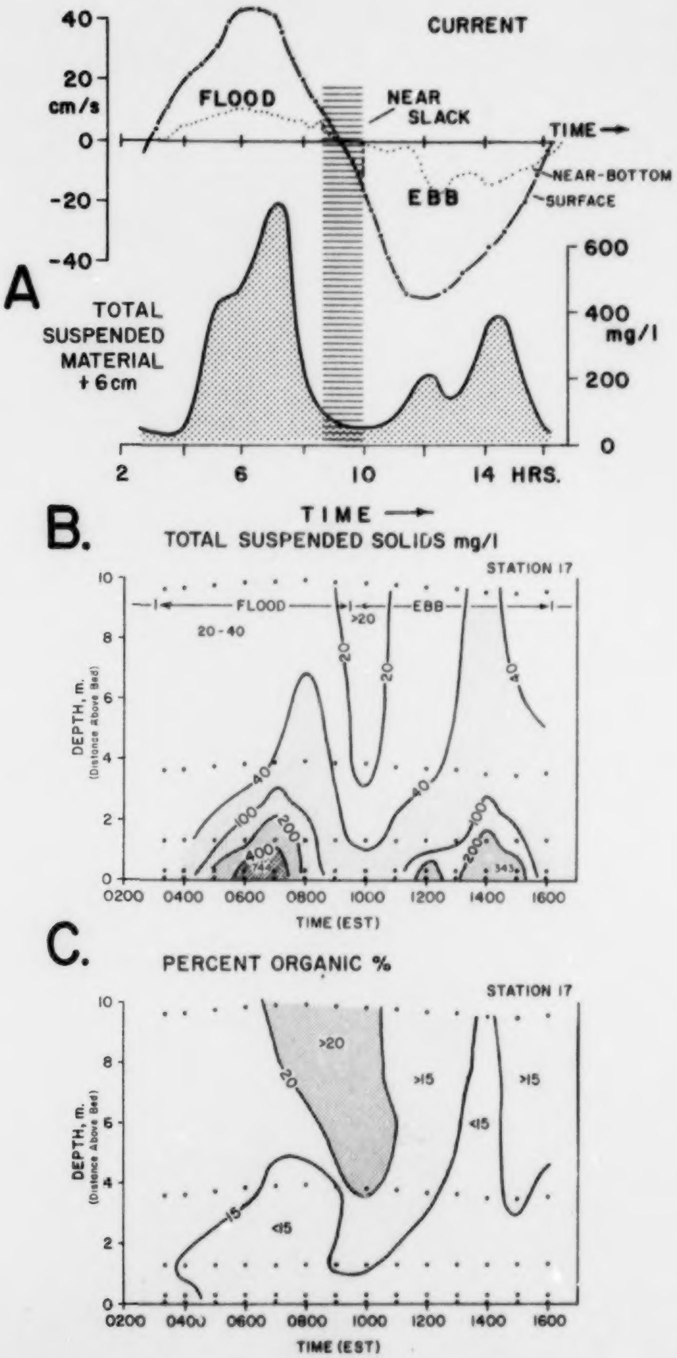


Figure 10. Temporal variation of total suspended material (solids)(B) and percent organic content with depth above the bed (C); anchor station 17, April 30, 1980.

of very fine-grained particles with a narrow size range. Its temporal and spatial variability of mean size is relatively small compared to the intermittently suspended load. With depth toward the bed, the resuspended load becomes coarser and more poorly sorted. As shown in Figure 10, percent organic matter is higher at slack water (23%) than at maximum current (14%). Because metal content can vary with suspended load, particle size and organic matter, it is subject to marked tidal variation.

TIME VARIATIONS OF METALS

As noted during earlier studies (cruises 1-4) of this project (20)(21), metal concentrations per liter of Bay water followed patterns set by mg/l suspended sediment -- especially in the region of the northern Bay turbidity maximum (stations 15-18). Per gram of suspended matter, metal trends over the 13-hour tidal cycles varied with station, depth, and with the particular metal of interest (see Figures 11-16). However, as noted in Table 7, suspended Fe, Mn and Zn remained uniform in the northern Bay both vertically (at the surface, mid-depth, and near-bottom) and between stations (as shown at 17 and 19) throughout the tidal cycle. Cu and Pb were more variable, as noted for Station 17, as was Fe at Station 11. Cd values were usually less than 3.5 μg/g at all stations and depths.

TABLE 7. EXAMPLES OF METAL CONCENTRATIONS PER GRAM SUSPENDED MATTER-TIME SERIES STUDY (mean ± standard deviation), OVER 13 HOURS.

Metal	Station	Surface	Mid-Depth	Bottom
Fe (%)	19	4.4 ± 0.8	4.0 ± 0.8	4.0 ± 0.5
Zn (mg/g)	19	.26 ± .05	.27 ± .11	.27 ± .08
Mn (mg/g)	19	3.6 ± 1.1	3.3 ± 1.0	3.5 ± 0.8
Fe (%)	17	4.3 ± 0.4	4.4 ± 0.3	4.2 ± 0.4
Zn (mg/g)	17	.32 ± .06	.32 ± .06	.27 ± .05
Mn (mg/g)	17	3.3 ± 0.6	3.4 ± 0.6	3.6 ± 0.5
Cu (μg/g)	17	71 ± 26	66 ± 13	49 ± 13
Pb (μg/g)	17	91 ± 33	91 ± 30	59 ± 23
Fe (%)	11	1.8 ± 0.8	0.5 ± 0.2 (8m) 0.9 ± 0.3 (16m)	1.4 ± 0.6

For the tidal cycles, specifically at station 11, surface suspended Fe concentrations (Fig. 11) decreased from 3.0% to 1.2% as the tides progressed from slack to ebb. At the 8 m depth, Fe concentrations varied little. For the 16 m depth, Fe concentrations peaked at 0500-0800 and 1100-1400 as the flood and ebb currents decreased below 0.6 m/sec. Near the bottom, sediment peaks in suspended Fe concentrations occurred at 0400-0700 and 1300-1500 as peak flood and ebb currents decreased to less than 0.2 m/sec. For Mn though (Fig. 11), surface suspended concentrations decreased from 4.1 mg/g to 1.7 mg/g at 0700-1000 corresponding to tidal currents changing from flood to slack. Yet, 8 m, 16 m, and near-bottom concentrations remained < 0.5 mg/g as flood and ebb currents dropped below 0.4 m/sec. Zn concentrations (Fig. 11), although showing more variability than either Fe or Mn, remained constant at 8 m, 16 m, and near-bottom depths during flood current velocities < 0.4 m/sec.

At station 15, near-bottom Cu, Fe, Mn, and Zn (Fig. 12) concentrations (per gram) showed little variation during flood or ebb tidal current < 0.2 m/sec. Fe and Mn, though, produced more cyclic characteristics depending on tidal phase -- i.e. flood, slack, or ebb.

As shown in Figures 13 and 14 for station 17, Fe (mean- 4.3%), Mn (3.4 mg/g), and Zn (0.30 mg/g) varied within narrow limits for all depths during flood and ebb surface currents up to 1 m/sec. As flood reached maximum at 0600, surface and mid-depth Pb concentrations (Fig. 13) decreased. From 0900-1100, surface and mid-depth Cu (Fig. 14) and Pb increased as maximum ebb was reached, decreasing afterwards.

For station 19 (Figs. 15 and 16), suspended Cu and Pb (Fig. 15) concentrations varied considerably, though Fe (mean - 4.1%) in Figure 15 and Zn (mean - 0.26 mg/g) in Figure 16 were constant from slack to ebb.

Several factors could be affecting suspended matter metal concentrations during a tidal cycle. Duinker and Nolting (34) noted the affect of salinity changes on metal concentrations during flood and ebb. Suspended Pb, Zn, and Fe concentrations increased with decreasing salinity, although Mn concentrations decreased and were least affected by particulate sedimentation processes. Schubel (35) discussed the affects of critical erosion speeds (35-50 cm/sec) of fine-grained sediments and the role of vertical mixing in spreading fluctuations in suspended sediment concentrations throughout the water column. Tidal currents in the northern Chesapeake Bay were found to also produce changes in particle size distribution near the bottom (35), (36), ranging from < 3μ near slack water to > 20μ at maximum flood and ebb, with coarsest particles nearest the bottom. Schubel, et al. (37) divided the suspended sediment

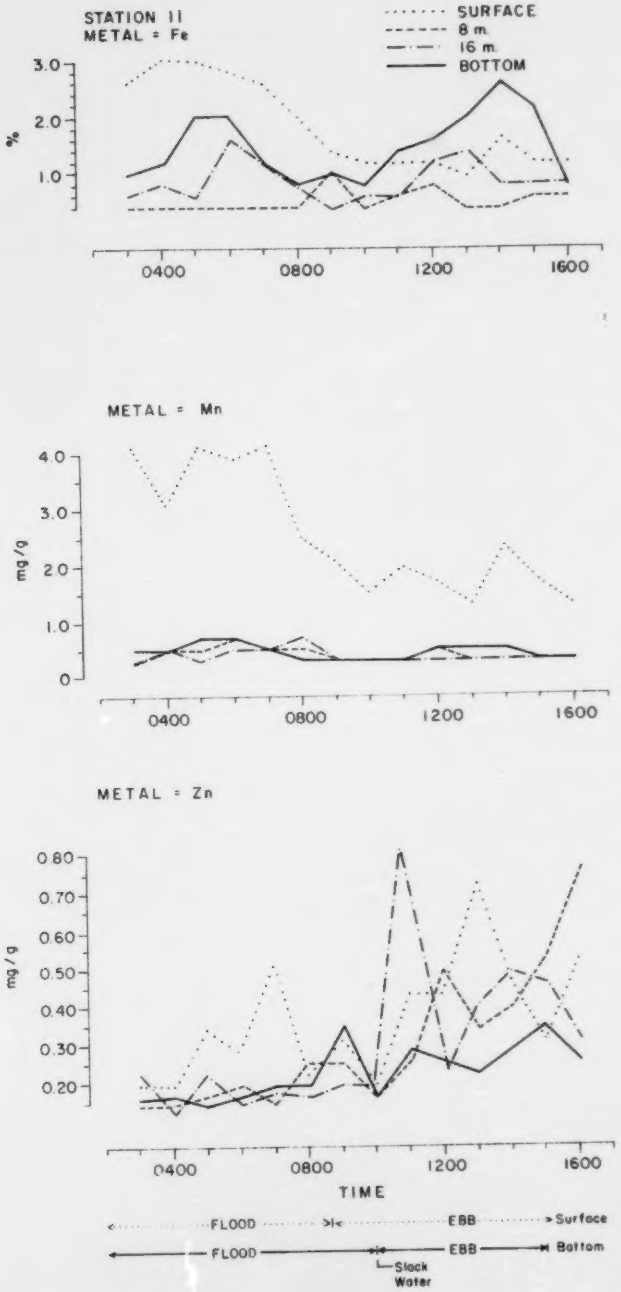


Figure 11. Temporal variation of Fe, Mn and Zn over a tidal cycle at station 11, northern Bay, May 2, 1980.

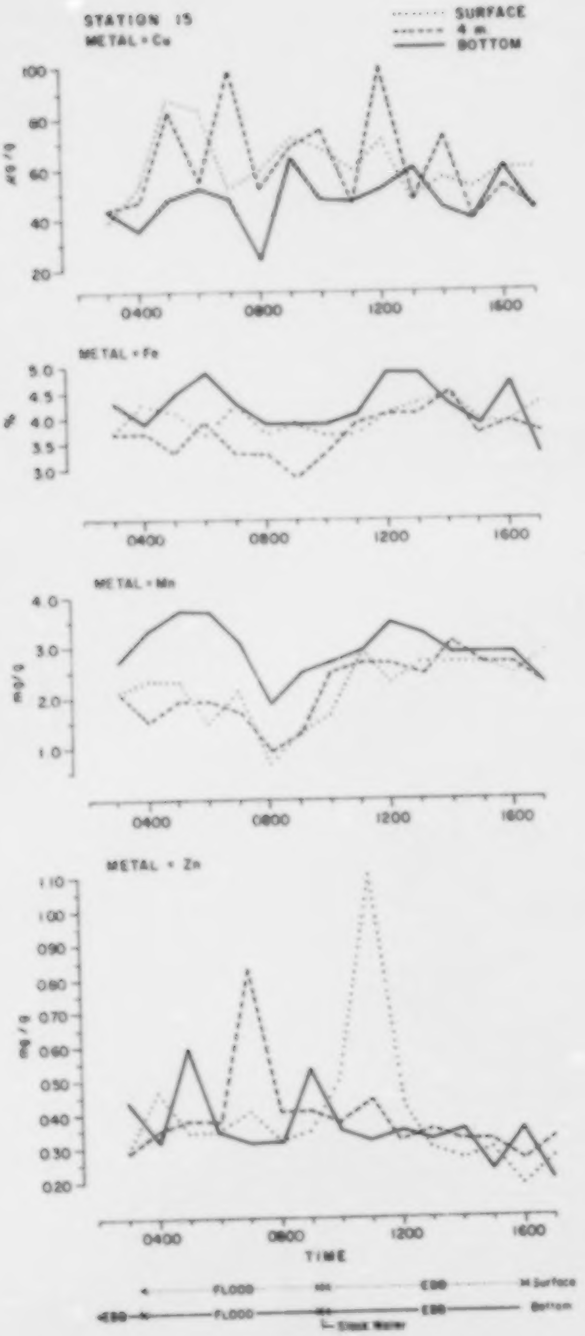


Figure 12. Temporal variation of Cu, Fe, Mn and Zn over a tidal cycle at station 15, northern Bay, May 1, 1980.

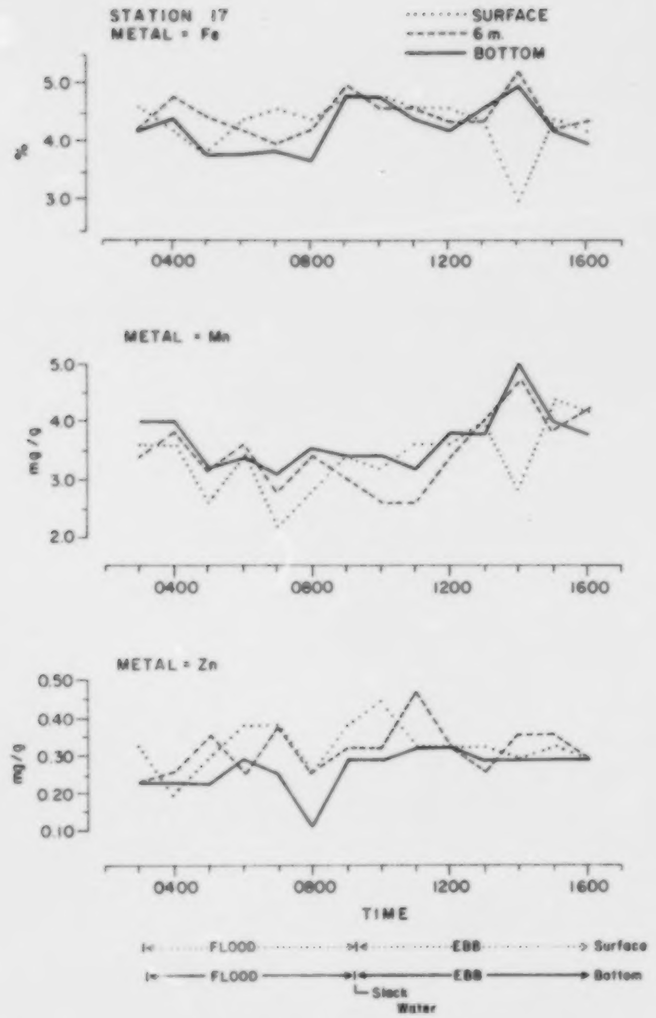


Figure 13. Temporal variation of Fe, Mn and Zn over a tidal cycle at station 17, northern Bay, April 30, 1980.

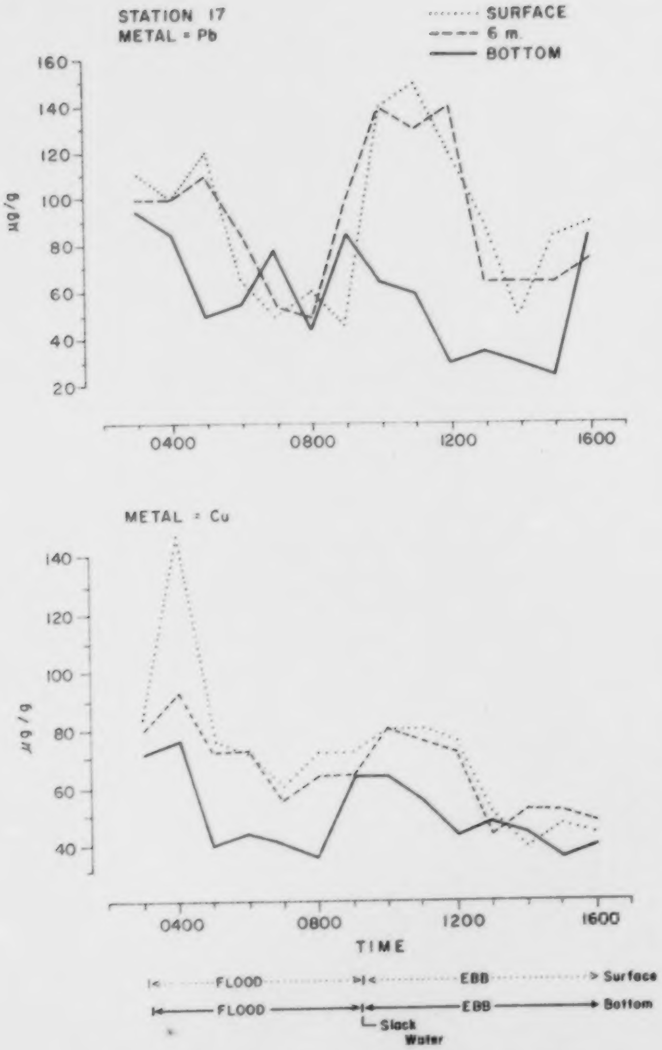


Figure 14. Temporal variation of Pb and Cu over a tidal cycle at station 17, April 30, 1980.

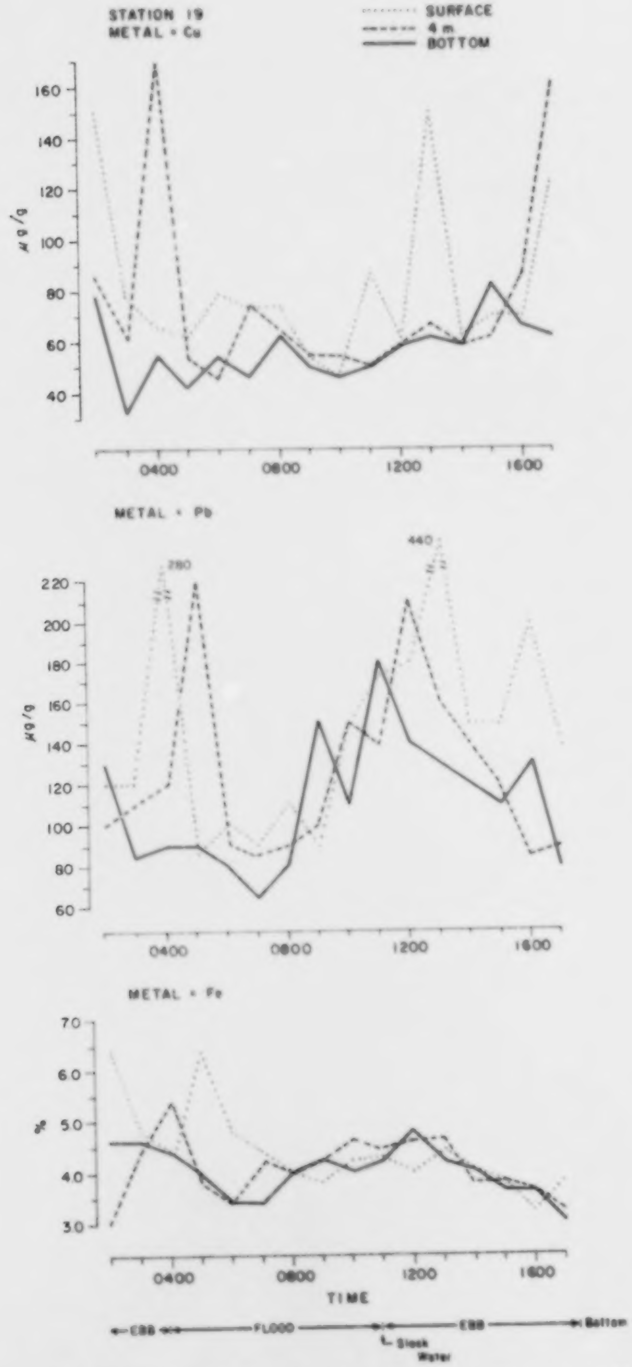


Figure 15. Temporal variation of Cu, Pb and Fe over a tidal cycle at station 19, April 29, 1980.

population of the upper Chesapeake Bay into sub-groups -- those particles continually suspended and those alternately suspended and deposited. Their analyses did not indicate any differences in size distributions of suspended sediment at similar current speeds and particulate concentrations during either ebb or flood, which of course, could affect observed metal distributions.

Metal concentrations were normalized to Fe since it is an indicator of mineral and oxyhydroxide components of suspended matter which can act as adsorbers. As noted in Table 8, station 11, metal to Fe ratios were consistently higher than the other stations sampled, except for Mn/Fe near the bottom. Similar increased ratios in the mid-Bay had been observed during cruises 1-4 in 1979, as noted during earlier discussions. Pb/Fe ratios at stations 15 and 19, surface and mid-depth, were higher and more variable than observed at the other northern Bay station (17) sampled. Bottom suspended matter ratios in this region were comparable to those earlier observed for fluid mud, reflecting the potential source of bed sediment resuspension and metal loads from the Susquehanna River (37). In the upper Bay (stations 15, 17 and 19), Cu/Fe and Zn/Fe ratios were similar among stations. The Mn/Fe ratio at station 11 bottom was quite low (.031 ± .011) compared to the enhanced surface suspended value (.14 ± .02) which varied little throughout the tidal cycle.

TABLE 8 . METAL CONCENTRATIONS NORMALIZED TO FE (mean ± standard deviation of ratios).

Station - Depth (m)	Cu/Fe (x 10^{-4})	Mn/Fe	Pb/Fe (x 10^{-4})	Zn/Fe
15-0	16 ± 3	.054 ± .015	54 ± 19	.010 ± .006
15-4	17 ± 6	.057 ± .013	43 ± 21	.011 ± .004
15-bottom	11 ± 2	.070 ± .008	24 ± 5	.009 ± .002
17-0	16 ± 6	.079 ± .014	21 ± 7	.007 ± .001
17-6	15 ± 3	.078 ± .013	21 ± 6	.007 ± .001
17-bottom	12 ± 3	.087 ± .010	14 ± 6	.006 ± .001
19-0	19 ± 7	.085 ± .034	39 ± 21	.006 ± .002
19-4	19 ± 9	.084 ± .029	32 ± 10	.007 ± .003
19-bottom	15 ± 4	.089 ± .018	28 ± 7	.007 ± .002
11-0	45 ± 23	.14 ± .02	110 ± 40	.026 ± .019
11-bottom	48 ± 22	.031 ± .011	82 ± 45	.018 ± .008

In summary, fluctuations of current strength over a tidal cycle produce large fluctuations in suspended loads and moderate fluctuations in particle size and percent organic content. Associated fluctuations of Fe, Mn and Zn (we./we.) vary within narrow limits whereas Cd, Cu and Pb vary widely, more than 2-fold. These short-term fluctuations combined with seasonal fluctuations of processes and source input make temporal trends of metals in the Bay highly variable.

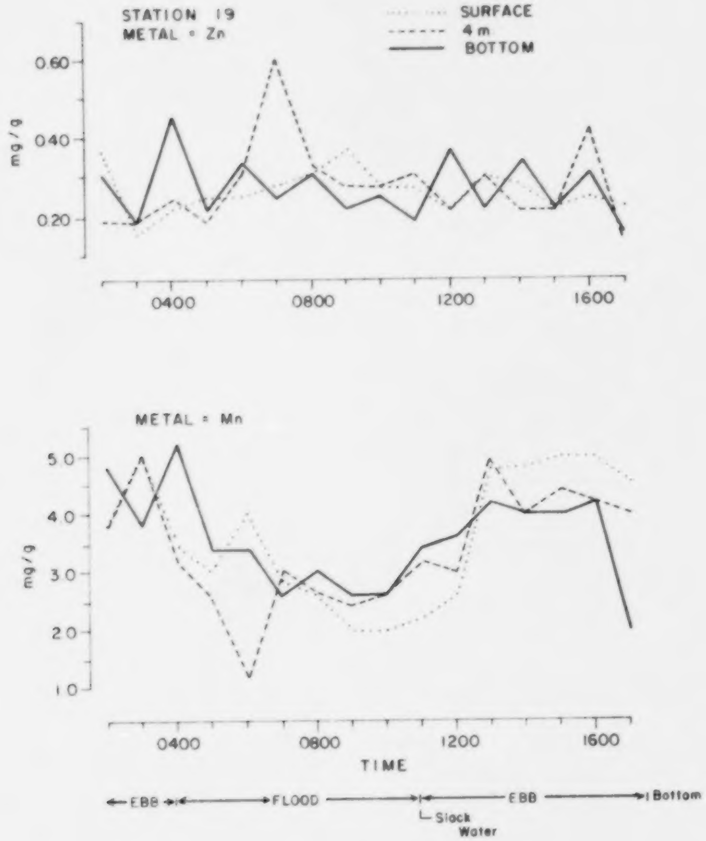


Figure 16. Temporal variation of Zn and Mn over a tidal cycle at station 19, April 29, 1980.

SECTION 6

INTEGRATION OF RESULTS

METAL INTERACTIONS AND CORRELATIONS

To account for spatial and temporal variations of the metal distributions and to predict the fate of metals that associate with each other or with sediment properties, a number of computerized statistical correlations were performed. Correlation coefficients (r) of 0.70 or larger are considered significant since these account for at least 50 percent of the covariations at the > 95% level (18)(19), and thus define metal associations. The correlations treat data for suspended material (1) at different depths and (2) for time series observations and all depths.

Suspended Material

For surface suspended material most correlations varied over wide limits. However, in data of cruises 1 and 2, March-April and May, 1980, Mn-Fe correlate (r=0.80) except for northern Bay stations of cruise 2 (20). Additionally, Cu-Zn and Ni-Zn correlate (r=0.80; r=0.74) respectively, except for mid-Bay and near-ocean stations of cruise 2 (i.e. numbers 1, 8, 9, 11, 12 and 13)(20).

In near-bottom suspended material from Bay-wide cruises 1 and 2, Mn and Fe correlated (r=0.81; r=0.80) but Cu is not highly correlated with Fe for different sampling cruises (Fig. 17A, 17B). However, Cu-Zn correlated (r=0.85; r=0.81, for cruises 1 and 2); Ni-Zn correlated (r=0.83; r=0.82 for cruises 1 and 2), Figures 17B and 17C. For selected stations from the northern Bay, stations 12-21, Ni-Fe correlated (r=0.77) and Zn-Fe correlated (r=0.79; r=0.87).

In the time series observations of suspended material, coefficients are significant for metal to metal correlations, e.g. Fe-Mn (r=0.71) at station 15; Cu-Pb (r=0.70) at station 17; and Fe-Mn-Pb (r > 0.80) and Cu-Zn (r=0.92) at station 11. Additionally, Pb partly correlates with mean size (r=0.67). Metal-metal correlations most likely result from particle adsorption on particulate matter.

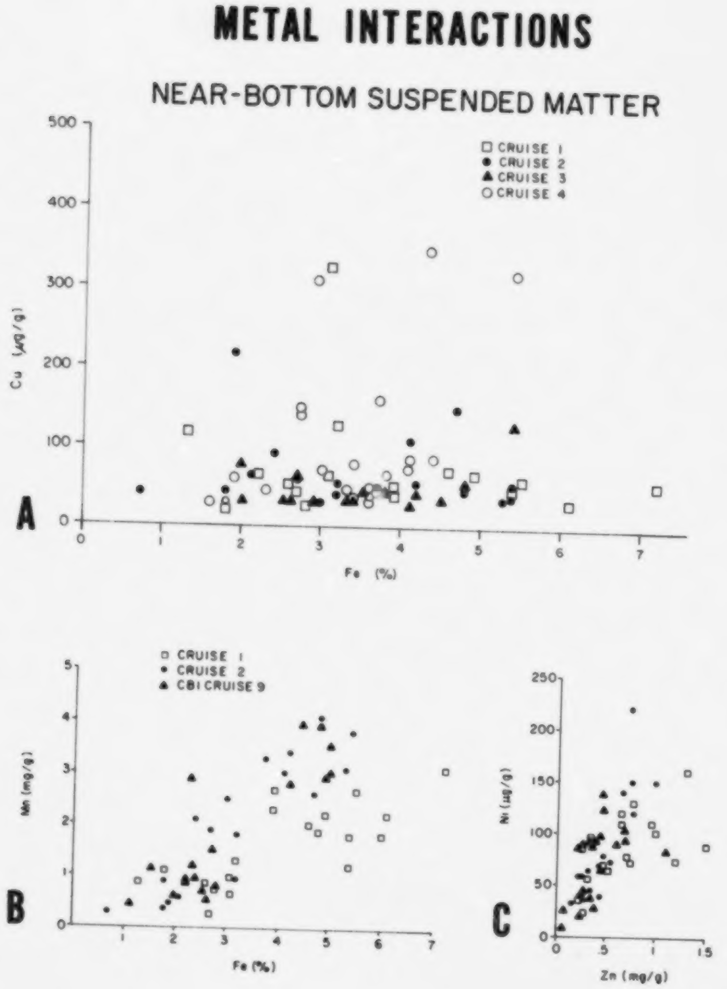


Figure 17. Metal-metal plots for near-bottom suspended material from cruises 1-4; (A) Cu-Fe, (B) Mn-Fe, (C) Ni-Zn.

When correlation coefficients are calculated for eleven different metals in relation to percent organic content, organic concentration and mean particle size (dispersed) of suspended material for all depths at selected longitudinal stations (11-19, 24) in the northern Bay, a few significant coefficients are revealed (Table 9). Most of the metals, however, did not correlate with suspended sediment characteristics. In general, the number of significant metal-metal, and metal-sediment characteristic correlations for suspended material is limited. Their persistence with time, e.g. season to season, is uncertain. The scant correlations may reflect varied sources of suspended material and selective metal utilization by different organisms in suspension. They support the contention that estuarine suspended material is non-conservative and unstable (38).

Bed Sediment

In Bay-wide bed sediments and fluid mud, significant metal-metal correlations occur between all metals except Hg, especially As-Fe, Cu-Fe, Ni-Fe, Pb-Fe and Zn-Fe. As shown in Figures 18A, 18B, Zn and Pb follow a near-linear trend in relation to Fe with the coefficients (r) recorded in the figures.

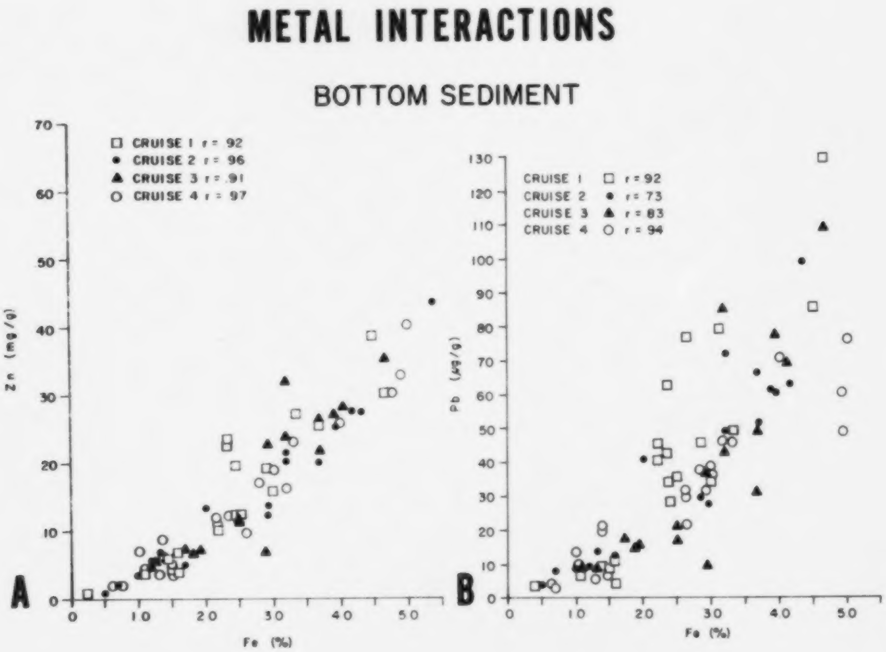


Figure 18. Metal-metal relationships for bottom sediment samples including fluid mud for cruises 1-4; (A) Zn-Fe; (B) Pb-Fe.

TABLE 9. CORRELATION COEFFICIENTS (r > 0.70) FOR METALS AND SUSPENDED SEDIMENT CHARACTERISTICS; CRUISE 4; STATIONS 11-19, 24; CRUISES 5 and 6, STATIONS 13-18, NORTHERN CHESAPEAKE BAY.

Metal	Organic Percent	Organic Concen. mg/l	Mean Size, μ
CRUISE 4			
Fe mg/l	0.73	0.76	
Ni μg/l	0.70		
Pb μg/l	0.74		
Fe %	0.81		
Hg μg/g	0.81	0.71	
CRUISES 5 and 6			
Fe %			-0.73
Cu	-0.86		
Pb μg/g	0.76		0.84
	0.70		
Zn mg/g	0.80		
*Cu/Pb/Zn	> 0.75		
*Fe/Mn	>-0.80		-0.71
**Cu/Pb/Zn	-0.96		

*For stations 13-19, 22, cruise 6.

**For stations 11-18, 22, cruise 5.

Fluid mud from anchor stations in the northern Bay, 15, 17 and 19, which contained metal concentrations within narrow limits (Table 9), showed significant correlations for Fe-Cu-Mn-Pb-Zn ($r > 0.80$).

METAL-FE RATIOS

Iron is a good element for normalizing unknown variables associated with other metals because it is abundant and human sources are small compared to natural sources. Additionally, iron concentrations vary within narrow limits along the Bay length and it has low solubility in the pH 7-8 range. Soluble Fe in the Bay is a very small fraction of the total load (10). Moreover, iron exhibits a significant correlation with aluminum, a relatively inactive element in Bay suspended material (32).

Mn-Fe and Zn-Fe ratios in bed sediment decrease with distance seaward (Fig. 19) away from the Susquehanna River, a major metal source. These trends are broadly similar to trends for mean Mn, Zn and Ni concentrations, Appendix 7. Of note are the elevated Mn-Fe ratios at stations 20, 21 near Baltimore Harbor, and at stations 3, 4, Hampton Roads.

Metal-Fe ratios in near-bottom suspended material, e.g. Cu-Fe, Pb-Fe and Zn-Fe for northern Bay stations 13-19, vary within narrow limits (Fig. 20). The ratios, Cu-Fe, Mn-Fe and Zn-Fe are comparable to those in fluid mud, a trend that can develop as the bed mud is repeatedly resuspended. This is confirmed by time series variations of ratios whereby Cu-Fe ratios are lower near maximum current than slack water. On the other hand, Pb-Fe ratios are higher in suspended material than the bed suggesting Pb is either released from the bed sediment or actively fractionated in suspended material. Elsewhere metal-Fe ratios of the central and lower Bay are much larger than in the northern Bay (Figs. 20, 21 and 22). With distance along the Bay length and from cruise to cruise, the ratios are highly variable. It is no wonder metal-metal correlations in suspended material from this zone are scant. Because organic content of suspended material is relatively high in the zone (Fig. 3C), it seems likely the high concentrations relate to organic detritus or plankton.

ENRICHMENT FACTORS

To organize the metal data for use as indicators of contamination, enrichment factors are derived by establishing baseline levels from standard crustal values of Turekian and Wedepohl (39). Both crustal values and observed values were normalized to Fe. Iron was used for the same reasons as noted earlier for Fe ratios. By ratioing Fe in shale to Fe in Bay sediment, and also the concentration of metal in shale, an "expected" value for Bay sediment is derived. A metal is taken as enriched if

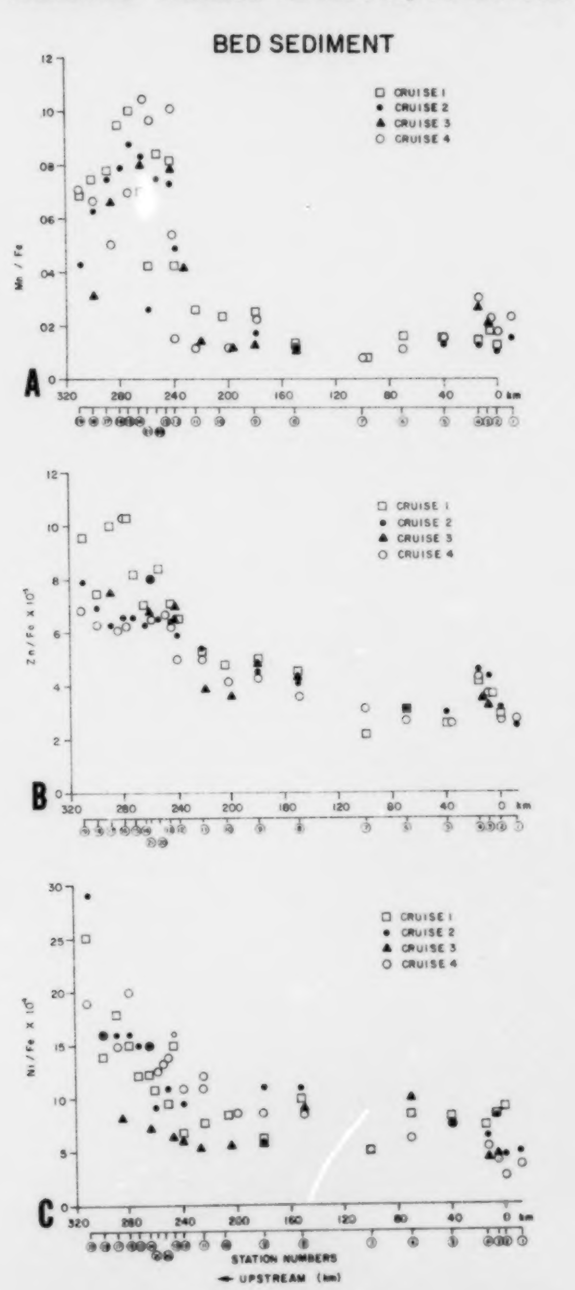
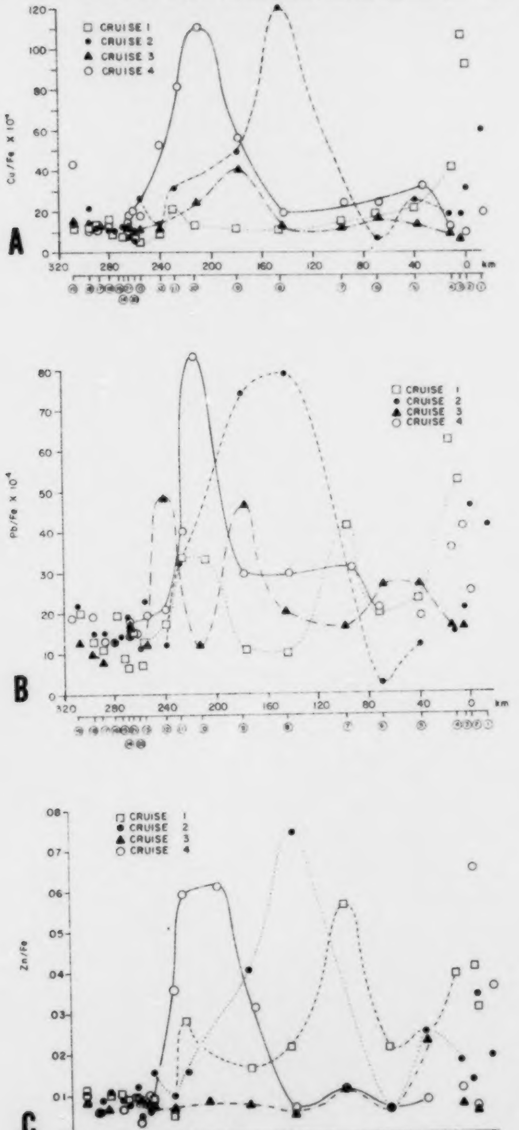


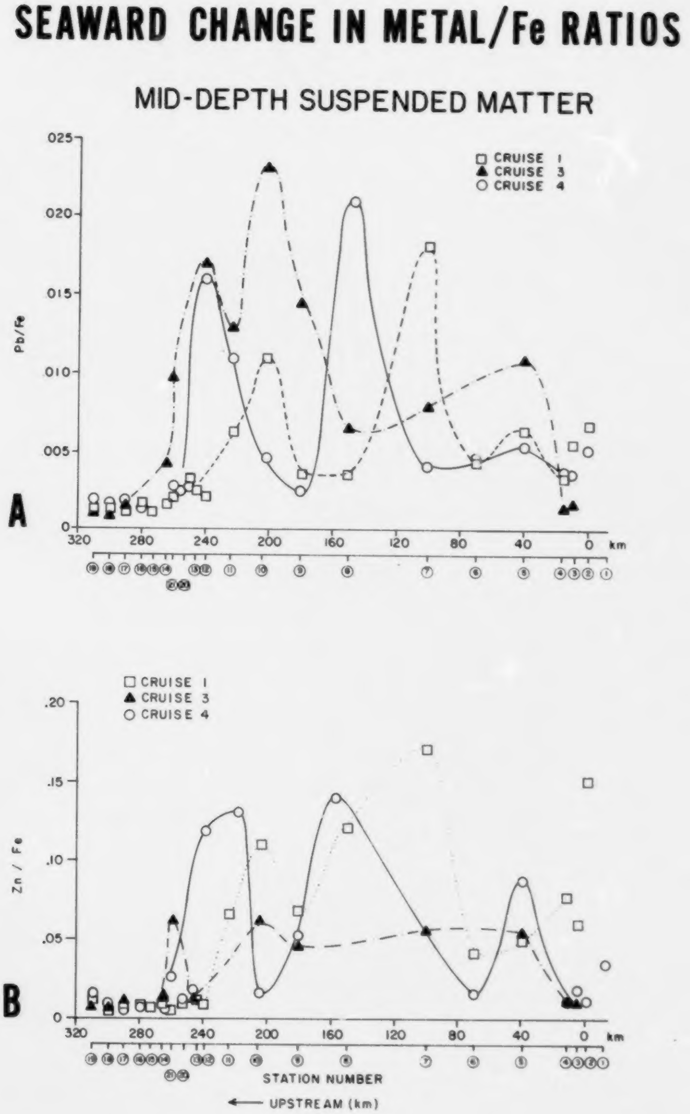
Figure 19. Metal-Fe ratios of bed sediment along the Bay length; (A) Mn/Fe; (B) Zn/Fe; (C) Ni/Fe.



SEAWARD CHANGE IN METAL/Fe RATIOS

NEAR-BOTTOM SUSPENDED MATTER

Figure 20. Metal-Fe ratios of near-bottom suspended matter along the Bay length; (A) Cu/Fe; (B) Pb/Fe; (C) Zn/Fe.



SEAWARD CHANGE IN METAL/Fe RATIOS

MID-DEPTH SUSPENDED MATTER

Figure 21. Metal-Fe ratios of mid-depth suspended matter along the Bay length; (A) Pb-Fe; (B) Zn-Fe.

SEAWARD CHANGE IN METAL/Fe RATIOS

SURFACE SUSPENDED MATTER

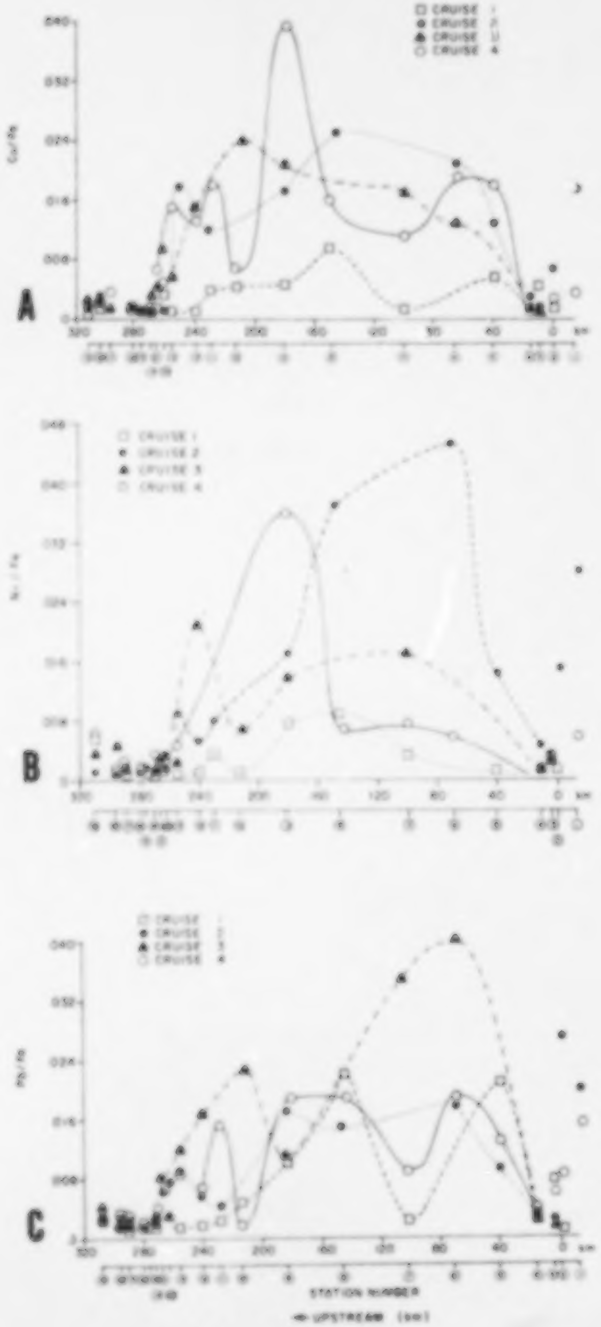


Figure 22. Metal-Fe ratios of surface suspended matter along the Bay length; (A) Cu/Fe; (B) Ni/Fe; (C) Pb/Fe.

the observed concentration exceeds the expected value. A factor of one implies no enrichment relative to crustal values. The relation is summarized as:

$$EF = \frac{(^{X}ob/Fe)\ \text{sediment}}{(^{X}ex/Fe)\ \text{shale}}$$

where $^{X}/Fe$ is the ratio of concentrations of metal (X) to Fe in the sediment and in the shale.

The advantage of a geochemical baseline level is that it provides a standard for comparing data throughout the Bay, and the Bay to other systems. It assumes a uniform crustal average throughout the region and that rock of the Chesapeake drainage basin and natural uncontaminated Bay sediment are representative of average crustal shale. Because the method is chemical, it is independent of sediment physical properties like particle size. It is affected, however, by compositional changes such as varying organic content. Therefore, interpretation of "excess" metal as anthropogenic in organic rich suspended material is of limited validity since organisms can be naturally enriched.

For fluid mud and bed sediment, the expected metal content of Bay sediments, derived from Fe corrected average shale, is illustrated for each metal and station in Appendix 7. Of note, observed values of mean As, Hg and Sn are less than expected, or deficient, throughout the Bay while Cu and Ni are normal in the northern Bay but deficient in the central and lower Bay. By contrast, observed Pb departs from baseline values seaward to station 8 with distinctly higher enrichment factors in the northern Bay reaching 4.6 at station 14 (Fig. 23A). A similar trend is evident for Zn which reaches a peak of 6.3 at station 16. Factors for Cd are variable but Mn is distinctly enriched in the northern Bay, stations 12-19. Therefore, Mn, Pb and Zn reflect major human sources in the Baltimore-Susquehanna River area. Enrichment factors for the Susquehanna suspended load are Mn, 7; Pb, 7; and Zn, Tables 8 and 11, (9) which are about the same as in the northern Bay. Therefore, northern Bay fluid mud and bed sediment, which is primarily supplied from the Susquehanna (12), is not notably enriched in Mn, Pb and Zn from additional sources as Baltimore Harbor.

For suspended material, the expected metal content of Fe corrected average shale is illustrated for each metal and station in Figures 6 and 7. In near-bottom suspended material, from the central Bay, stations 8-11, Cd, Cu, Pb and Zn depart substantially from Fe corrected average shale. Factors for mean concentrations range 8 to 33 for Cd, 6 to 9 for Cu, 6 to 13 for Pb, and 9-13 for

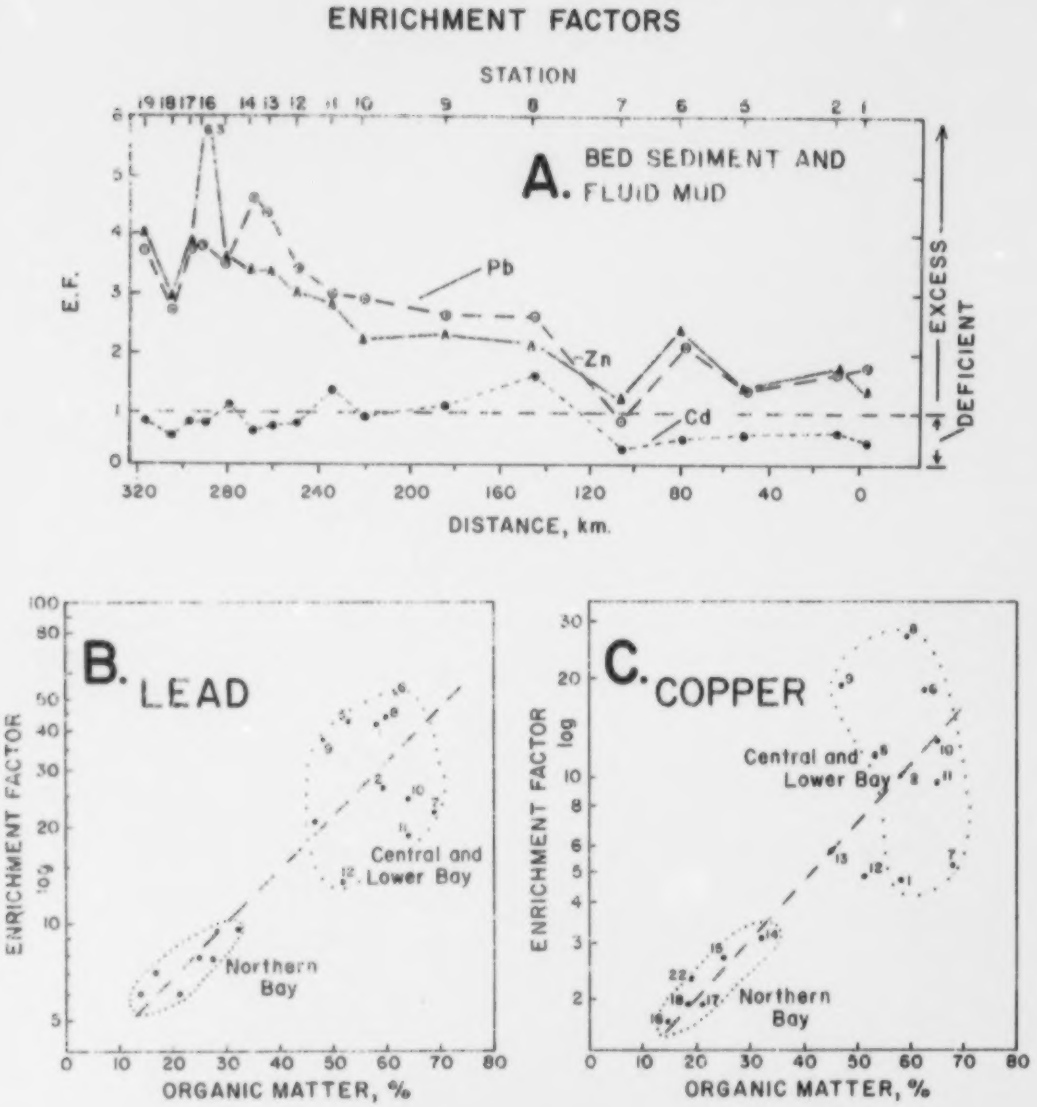


Figure 23. Variation of enrichment factors: (A) For Cd, Pb and Zn in bed sediment and fluid mud along the Bay length; (B) Lead enrichment factors versus percent organic matter for surface suspended material; (C) Copper enrichment factors versus percent organic matter for surface suspended material. Numbers represent station numbers.

Zn. Factors are higher in the central Bay than farther seaward or landward except for Mn and Pb that are slightly greater in the northern Bay than in the central Bay.

Departures from Fe corrected average shale for surface suspended material are much higher than in near-bottom suspended material (Figs. 6 and 7). In particular, Cd, Cu, Pb and Zn are higher in the central Bay, stations 5-10, than elsewhere. These compare with near-baseline values for As, Ni and Sn in the northern Bay. The high central Bay departures are indicative of high enrichment. Factors range 10-118 for Cd, 12 to 27 for Cu, 37 to 51 for Pb and 16 to 74 for Zn. The large departures and high factors occur in a zone of high percentage organic matter in the central Bay, especially in surface water, Figure 3. This trend is confirmed by graphs, Figures 23B and 23C, whereby enrichment factors for Pb and Cu generally increase with an increase of percent organic matter. The trend is linear for northern Bay stations 13-22, suggesting a detrital source of both metals and organic matter. Values for the central and lower Bay (stations 1-12) with relatively high factors, high organic content and substantial scatter, can be produced by metabolism of plankton. Whatever the cause, the relationship differentiates two distinct sub-groups of factors throughout the Bay, those from a northern zone and those from the central-lower zone.

It is useful to gain an estimate of relative enrichment by comparing observed metal concentrations with those of oceanic plankton from uncontaminated areas. Table 10 shows that metal content of Bay water exceeds the content of both phytoplankton and zooplankton more than 9 times for Cd and Zn, more than 19 times for Ni, Cu and Pb. Therefore, the impact of human and/or natural metal input, whatever its source, is affecting Bay suspended material on a regional scale.

When enrichment factors of Bay bed sediment are compared to other coastal systems, Table 11, it is noted that northern Bay sediment is enriched with Mn, Pb and Zn to a lesser degree than the Hudson and Delaware Estuaries but mainly more than San Antonio Bay and Galveston Bay. Mn is higher in the Chesapeake than elsewhere. In suspended material, enrichment factors for Cd, Pb and Zn are higher than the Rhine and all other areas compared, despite greater industrialization of other areas. This trend probably reflects greater planktonic production of the Chesapeake Bay.

TEMPORAL VARIATIONS AND LONG-TERM CHANGES

Samples collected approximately bi-weekly by the U.S. Geological Survey at Conowingo dam on the Susquehanna River during 1979-1980 show that concentrations of Fe and Mn (weight per volume) generally vary with variations of total suspended

TABLE 10. METAL CONTENT OF AVERAGE MARINE PLANKTON ON A DRY WEIGHT BASIS, μg/g

Metal	Chesapeake Bay Central & Lower Stations 6-11, mean surface	Oceanic Phytoplankton	Oceanic Zooplankton
Cd	26.8	2.1[3]	1.9-2.9[4]
Cu	225	7.1[3]	7.5-8.9[4]
Mn	2300	8.5[1]	1.1-7.8[2]
Ni	150	3.0[3]	2.8-7.8[4]
Pb	210	4.0[3]	1.2-8.5[4]
Zn	1300	38[3]	86-135[4]

[1] From Bostrom, et al. (40).

[2] From Förstner and Whitmann (13).

[3] From Förstner (41).

[4] From Trefy and Presley (42).

material and with river inflow. As shown in Figures 2 and 24, concentrations of suspended Fe at high inflow are more than 20 times the concentrations at low inflow while corresponding suspended Mn is more than 15 times. Similar data obtained by Carpenter (9) in 1966 suggest that other metals may follow these trends, however, there are exceptions. The metal Mn, for example, exhibits marked seasonal changes in partitioning. Suspended Mn is more dominate than soluble Mn in spring, summer and fall, a trend associated with influx of decaying organic matter in winter (9). It seems likely that seasonal changes in metal content (weight per volume) occur in the turbidity maximum zone seaward to Tolchester (station 14). The reason for this is that the metal-sediment concentration relation, e.g. for Fe, Figures 8A, 8B, for Susquehanna samples persists in the turbidity maximum zone (e.g. Fig. 8A). By contrast, Zn-suspended sediment values (Fig. 8B) display substantial scatter in the turbidity maximum and depart from the linear trend of Fe, a trend suggesting chemical or biological changes in the Bay. Eaton (10) shows relatively constant Fe concentrations in surface water and similarity to Susquehanna concentrations extending 60-80 km seaward from the river (vicinity station 13 of this study). Farther seaward, however, changes relating to fluctuations of river inflow were not observed in this study.

TABLE 11. COMPARISON OF ENRICHMENT FACTORS IN DIFFERENT COASTAL AREAS. FACTORS DERIVED FROM Fe CORRECTED AVERAGE SHALE

Area	As	Cd	Cu	Mn	Pb	Ni	Zn
Bed Sediments							
Chesapeake Bay,							
Northern, Stations 15-22	0.4	0.7	1.1	3.9	3.5	1.0	3.7
Central & Lower, Stations 2-10	0.8	0.7	0.5	1.1	2.0	0.5	1.9
Baltimore Harbor Stations 20, 21, 23	0.3	0.5	1.6	3.1	5.1	0.7	3.6
San Antonio Bay		1.1	0.4	1.1	2.2	0.7	1.6
Galveston Bay		5	2.8	3.2	8	2	3.6
San Francisco Bay			1.4	0.6		1.4	1.3
Hudson Estuary			2	2.0	9.0		4
Delaware Estuary		17	2		16	13	10
Suspended Sediments							
Chesapeake Bay,							
Northern, Stations 15-22	0.8	11	2.1	4.5	7.2	1.3	7.4
Central & Lower, Stations 2-10	4.4	76	14	7	35	5.8	45
Baltimore Harbor Stations 20, 21, 23		19	4	11	12	1.2	13
Susquehanna River, Conowingo		11	2	7	7	3	8
Rhine River, Waal		39	10	3.6	30	1.1	18
Rhine Estuary, HuH		11	2.4	2.3	13	0.9	6
Wadden Sea			34	3.8			40

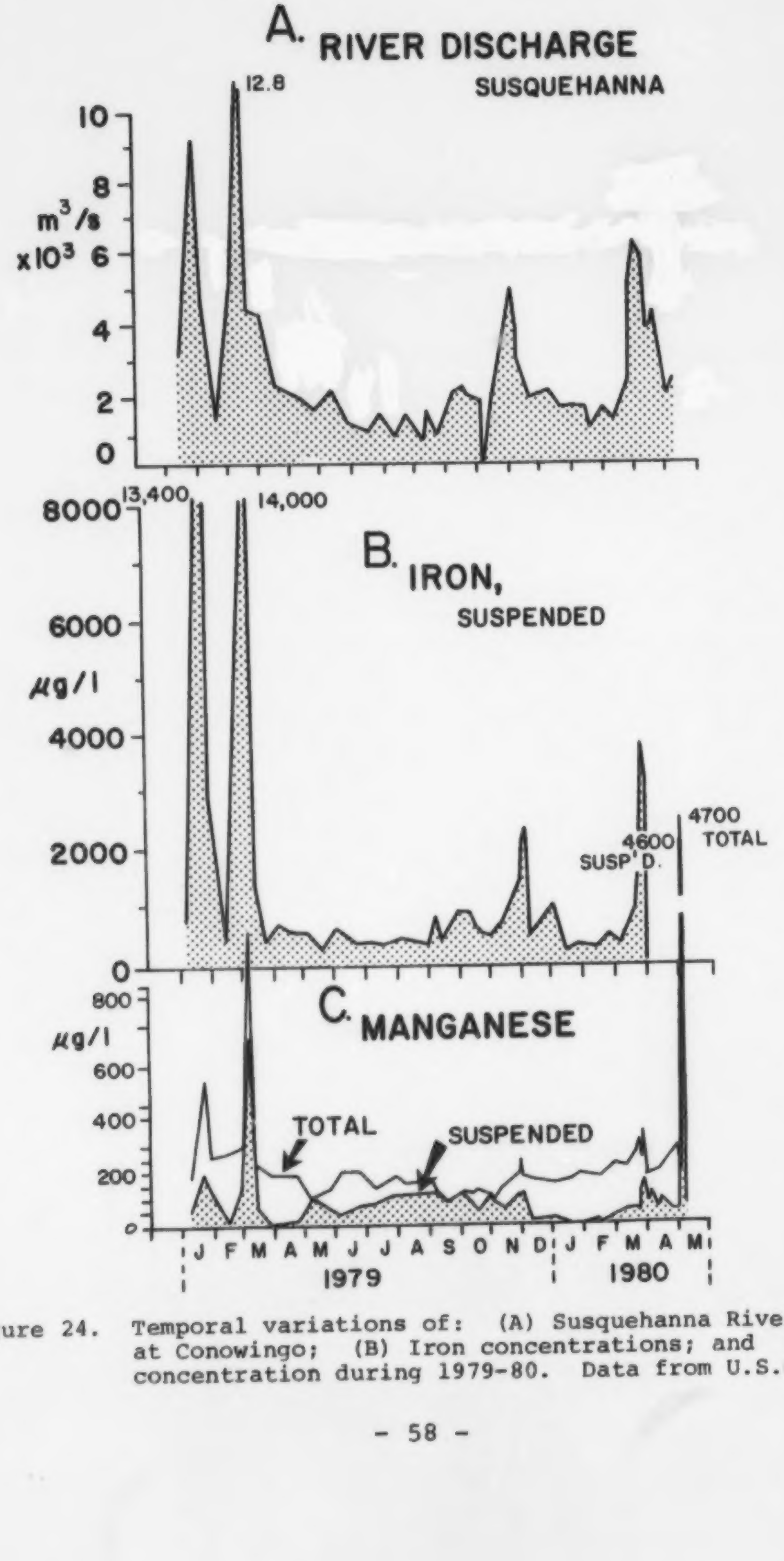


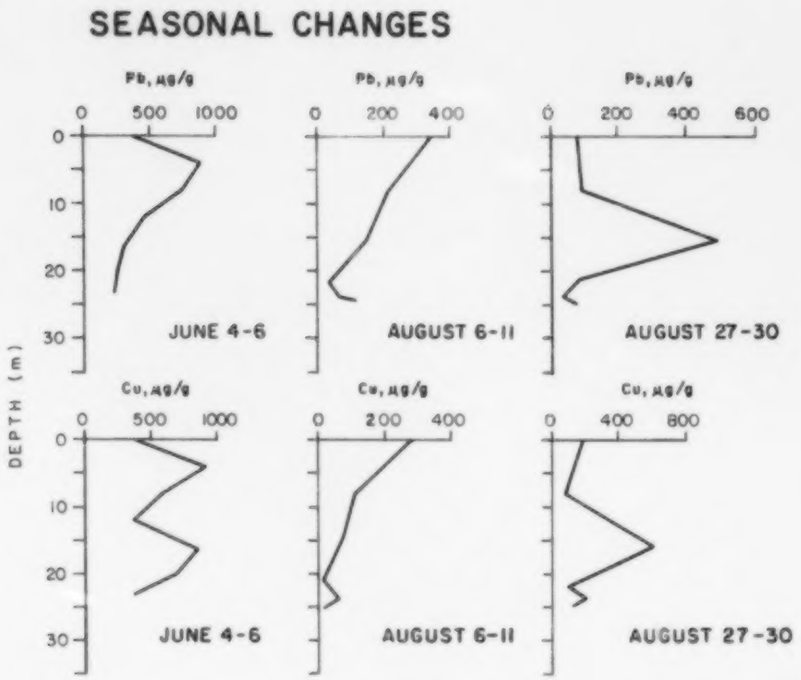
Figure 24. Temporal variations of: (A) Susquehanna River inflow at Conowingo; (B) Iron concentrations; and (C) Mn concentration during 1979-80. Data from U.S.G.S. (23).

When metal content (weight per volume) of samples collected at contrasting conditions of neap and spring tides is compared (21), e.g. cruise 3, August 6-11 (spring) and cruise 4, August 27-30 (neap), differences are evident in the zone of the turbidity maximum. River inflow during these periods was low and relatively constant. For example, Cd, Pb, Mn and Zn are more than 3 times greater at spring tide than at neap tide. This increase relates to the greater amount of suspended material at spring tide created by high bed resuspension. Elsewhere, the differences are very small or indeterminate because metal content varies widely.

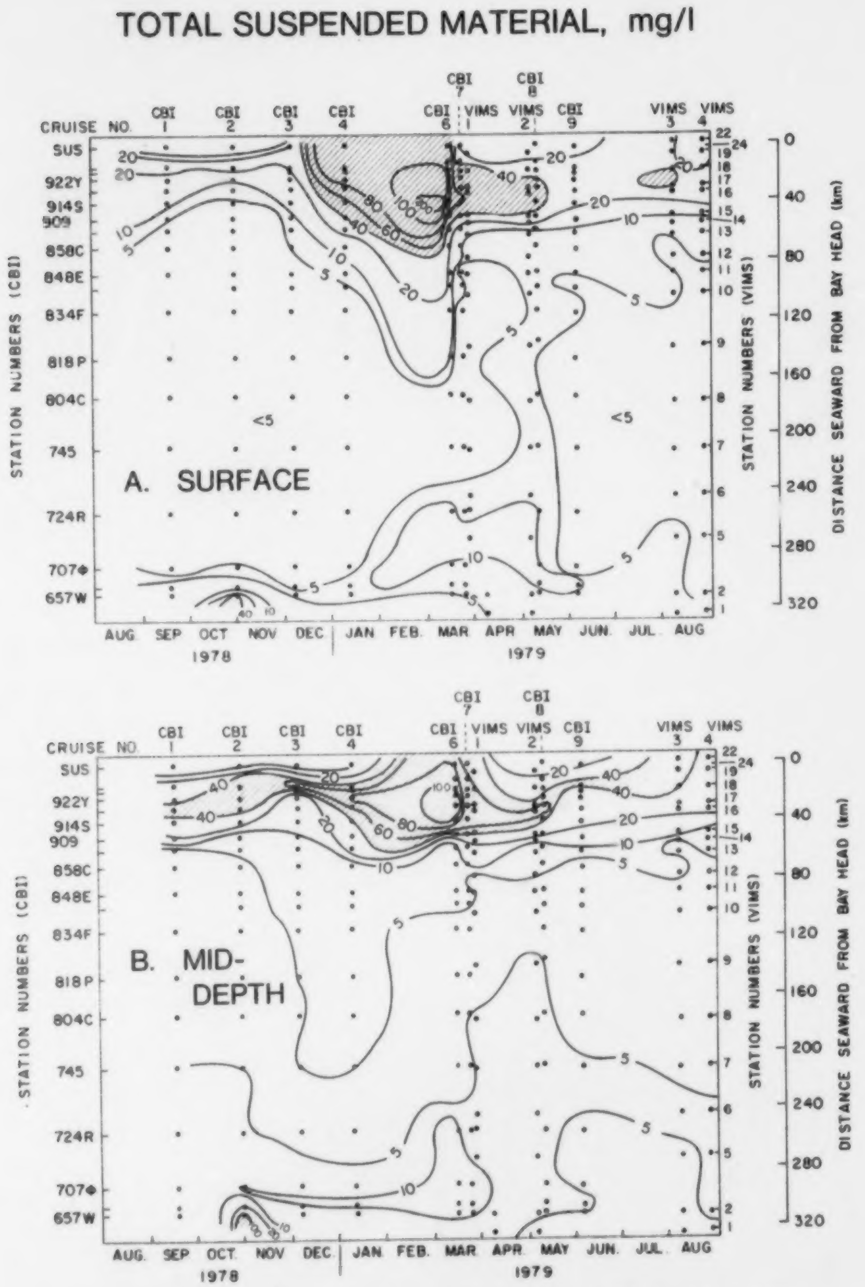
Metal concentration differences associated with contrasting oxygenated and anoxic water are exemplified by data from cruise 2, May 2-10 and CBI cruise 9, June 4-6, 1979. When near-bottom waters changed from oxygenated (2-5 ppm dissolved oxygen) to nearly anoxic (less than 1 ppm), the Cd, Cu and Pb content (we. per we.) increased more than 2-fold whereas the Mn content diminished by more than 3-fold. The latter change is partly confirmed by lower Fe/Mn ratios that diminish 2 to 8 times suggesting a loss of particular manganese relative to iron. Presumably the manganese is reduced and released into its dissolved state.

Seasonal differences from late spring (cruise 9) to summer (cruises 3 and 4) are revealed by vertical profiles for Cu and Pb, Figure 25. In late spring, a time of plankton blooms and relatively high chlorophyll a content in near-surface water, the concentrations of Pb and Cu (we. per we.) are about 2 times greater than in early August, cruise 3. A further reduction is noted near the surface in late August, cruise 4.

By integrating the monthly data for total suspended material collected and analyzed by CBI with those collected by VIMS using similar techniques during 1979-80, an annual cycle of changing suspended concentrations is revealed. As shown in Figure 26, greatest concentrations occur in the northern Bay landward of stations 858C or 12, during Jan.-April, a period of high river inflow (Fig. 2). Mid-depth concentrations in this zone, i.e. greater than 40 mg/l, persist throughout the year. Note that these concentrations are largely greater than farther landward near the river source. Concentrations in the central Bay are relatively low throughout the year. Surface values ranged 1.0 to 6.7 mg/l and mid-depth, 1.0 to 7.0, with higher concentrations in early May than at other times. Most of this material consists of organic matter produced by plankton. Near the Bay mouth, a localized aureole of 40-100 mg/l is noted, Oct.-Nov., 1978, as also a zone greater than 10 mg/l between Dec. and May. Organic matter is low to moderate and there are no other sources of fine sediment except from the Bay floor. It is likely that these concentrations result from bed resuspension.



25. Vertical profiles of Pb (upper) and Cu (lower) content illustrating changes in near-surface water of the central Bay from late spring to summer. June 4-6, CBI station 843F; Aug. 6-11, VIMS station 12, cruise 3; Aug. 27-30, VIMS station 12, cruise 4.



26. Distribution of total suspended material along the Bay axis from August 1978 through August 1979: (A) surface; (B) mid-depth. Zone of the turbidity maximum, shaded.

When these distributions are compared with a similar set of data for 1969-70, reported by Schubel and Carter (1), it is evident that the turbidity maximum has an increased load and is more persistent in 1978-79. Additionally, the 10 and 20 mg/l isopleths extend about 80 km farther seaward between the months of September and March. River inflow during the 1969-70 period averaged 1020 m^3 per sec while during the 1978-79 period it averaged 1280 m^3 per sec. Sediment influx for 1969-70 averaged 1.07^{106} metric tons; however, comparable data for the complete 1978-79 period are not available, at least from U.S.G.S. It can be inferred from the inflow data that 1978-79 was not an unusual year for sediment influx and probably followed inflow levels for 1978-79 which were close to the long term average, 985 m^3 per sec.

In summary, the largest temporal variations are produced by seasonal changes in river inflow and by organic accumulation in near-surface water. River inflow produces variations mainly in near-river reaches and together with spring-neap tidal resuspension, it secondarily affects the turbidity maximum zone. Summer anoxic of near-bottom water in the central Bay produces chemical conditions favoring release of Mn, while late spring plankton blooms in near-surface water can favor bioaccumulation of Cu and Pb.

SECTION 7

IMPLICATIONS OF RESULTS

SIGNIFICANCE OF FLUID MUD AND SUSPENDED MATERIAL

Suspended material does not settle directly to the bed but undergoes repeated cycles of resuspension and settling. Over the long-term, net downward movement leads to a loose watery structure of dense suspensions with high concentrations in the range 10-480 g/l. Vertical concentration profiles display a sharp change at about 5-20 g/l and form a high vertical gradient or interface. This is commonly taken as the mud-water interface. Although the concentration gradient is stratified, turbulent stresses of currents and waves can make the interface unstable, especially during storms. As a result surface mud is mixed with overlying water, affording an opportunity for chemical exchange and migration of constituents. Examples of fluctuating sediment concentration and metal content relating to resuspension and settling are provided in the section, tidal time series. These data show that fluid mud and suspended material are interrelated through dynamic processes.

Sediments that accumulate in the form of fluid mud are important for a number of reasons. First, they tend to accumulate in less energetic parts of the Bay, the axial basin, harbors, backwater embayments and the shipping channel floor. These zones are also favorable for accumulation of metals because they tend to have high clay content, substantial organic content and they are fine-grained. Additionally, they are zones of relatively fast deposition. High water content is maintained in the mud when the rate of deposition exceeds the rate of consolidation, a process that results in dewatering of the sediment. Because the mud accumulates at relatively high rates, it is more sensitive to metal inputs than non-fluid mud sediment. As shown for Kepone contaminated sediment (43), fluid mud was contaminated first, and it was also decontaminated first after input was arrested.

Fluid mud is important from the physical viewpoint because it fills shipping channels and harbors, and thus necessitates frequent dredging. In turn, disposal sites are required for placement of material in a watery state. This state is conducive to dispersal of large masses of material as mud flows and it is a poor substrate for benthic organisms. Commonly, more than 95 percent of the sediment mass discharged from an open water dredge pipe is in the form of fluid mud; only a small percent is released as suspended sediment into the water.

From the geochemical viewpoint fluid mud is important because its metal content (we. per vol.) is much greater than in suspended material. For example, at station 13 with a mean water content of 369% wet weight and mean bulk density (dry weight) of 1.19 g/cc, the equivalent sediment concentration is 300 g/l. The mean metal content of Pb in the mud is 59.8 μg/g which exceeds that in overlying water (30 cm above the mud-water interface) averaging 3.46 μg/l by 5,200 times.

Natural accumulations of fluid mud can move either by erosion of the surface and resuspension as suspended material in the water column, or as sheets and mud flows along the bottom. Although our multi-frequency acoustical equipment (at 22.5 and 200 kHz) defined numerous fluid mud layers, its possible movement as sheet flows less than 10 cm thick could not be detected within limits of equipment resolution. Additionally, movement could not be measured by Marsh-McBirney electromagnetic current meters within 6 cm of the mud-water interface because of interference produced by vertical stratification of the mud and suspended material. Nonetheless, X-ray radiographs of fluid mud box cores often display a fine structure of flaser-like bedding indicative of deposition from very high suspended loads. Because fluid mud bears a very high metal content (we. per vol.) the proportion of metals transported by the mud could be significant. The long-term stability and possible episodic movement during storms remains to be observed and understood.

PATHWAYS

Metals can be transported from their source to their sink along two principal pathways: (1) a hydrodynamic route; (2) a bioecological route. The probable hydrodynamic routes are sketched from: (1) direct current measurements with suspended material and metal content at four anchor stations in the turbidity maximum zone; (2) dispersion patterns of metal content in suspended material, fluid mud and bed sediment.

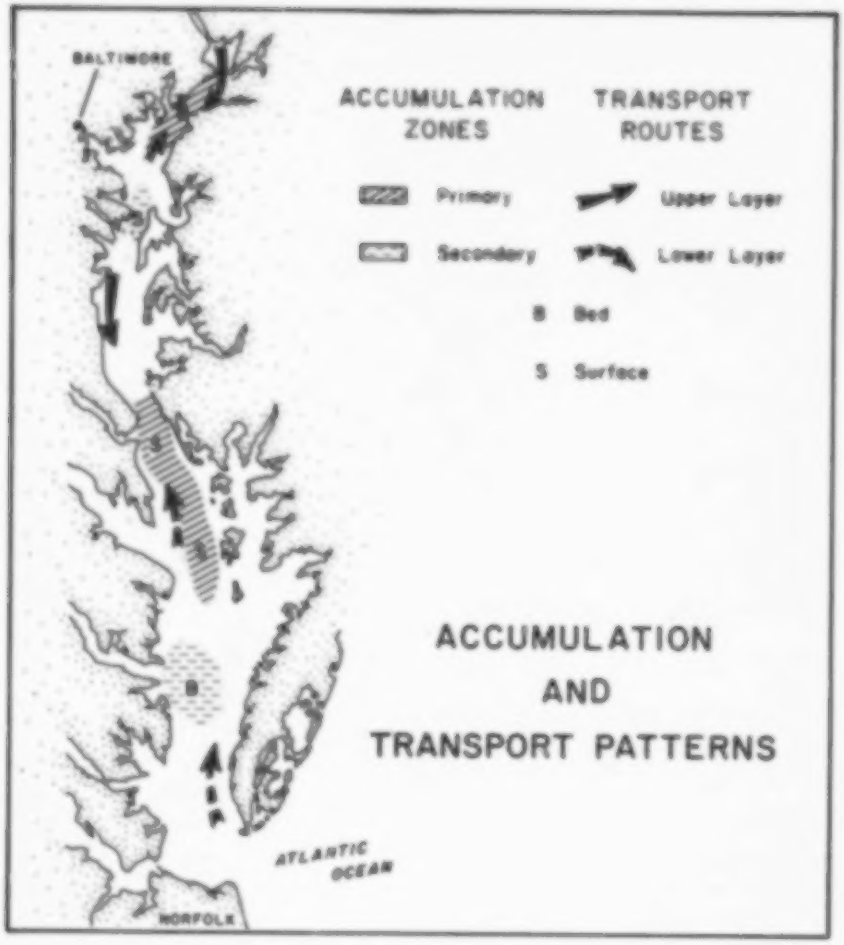
When metals enter the Bay with suspended sediment, which is released by natural soil erosion or discharged directly into the Susquehanna River in contaminated effluents, it is transported seaward through the freshwater reach of the Bay head. In this zone, it is diluted, dispersed by diffusion and advection and mixed with less contaminated suspended material. These processes act to reduce the initial metal concentrations. Transport in this reach is probably a transit process whereby much sediment and metals are moved quickly during short periods of high inflow and very slowly during long periods of moderate to low inflow.

As suspended material is flushed seaward into the fresh-salt transition, its seaward movement slows and much suspended material is trapped near the bottom in the null zone or convergence of seaward flowing river water and landward flowing salty Bay water. Some material, the clay size material and less dense organic material that stays in suspension in upper parts of the water column, can move farther seaward through the upper layer of the estuarine circulation. However, in seaward areas some of this material may settle, aided by particle agglomeration, and become entrained in the landward moving lower layer. When this material approaches the inner limit of salty water, transport is retarded because the net flow in this zone approaches zero. For material that settles faster than it is mixed upward by turbulence and salt exchange, there is net accumulation on the bed. But material that remains in suspension for long periods can be mixed upward and recycled seaward in the upper layer. Chemical changes are superimposed on physical transport whereby Fe and Mn for example can precipitate while metals in solution can be adsorbed. In contrast, if river-borne metals remain in solution or are desorbed, they likely flush through the convergence zone in the upper layer. They can escape the Bay through the upper layer or be taken up by plankton and then be consumed by fish.

Transport routes through the central Bay are revealed from metal patterns (44) showing seaward transport may take place along the west side of the Bay. This zone has a greater potential source of contaminates compared to the east side, but the route is compatible with the salinity regime and the path expected from the estuarine circulation.

Landward transport through the lower Bay is indicated from metal distributions of chromium (44) which extend landward from the Bay mouth along the eastern side. It seems likely that this transport extends farther landward through the lower estuarine layer of the central Bay. Figure 27 summarizes schematically probable hydrodynamic transport routes in relation to accumulation zones.

Relationships between sources of metals and accumulation zones are clearly complex. Not only are the sources unknown according to metal species or metal ratios, but the extent to which a measured concentration reflects natural and human sources in runoff as distinct from metal fluxes produced in the water by bioaccumulation or by resuspension from the bed (recycled) is unknown. Figure 28 provides a schematic and over-simplified representation of multiple paths of a metal supplied from a major fluvial source like the Susquehanna. Metals adsorbed to suspended material can enter the bioecological paths via suspension feeders, bacteria, plankton and fish. Once settled to the bed, sediment can be consumed by deposit feeders and their excretion products can be resuspended. The bioecological paths are


BALTIMORE
ACCUMULATION ZONES
TRANSPORT ROUTES
Primary
Secondary
Upper Layer
Lower Layer
B Bed
S Surface
S
S
B
ACCUMULATION AND TRANSPORT PATTERNS
ATLANTIC OCEAN
NORFOLK

27. Schematic diagram showing primary and secondary zones of metal accumulation in fluid mud, bed sediment and suspended material. Arrows represent likely transport routes.

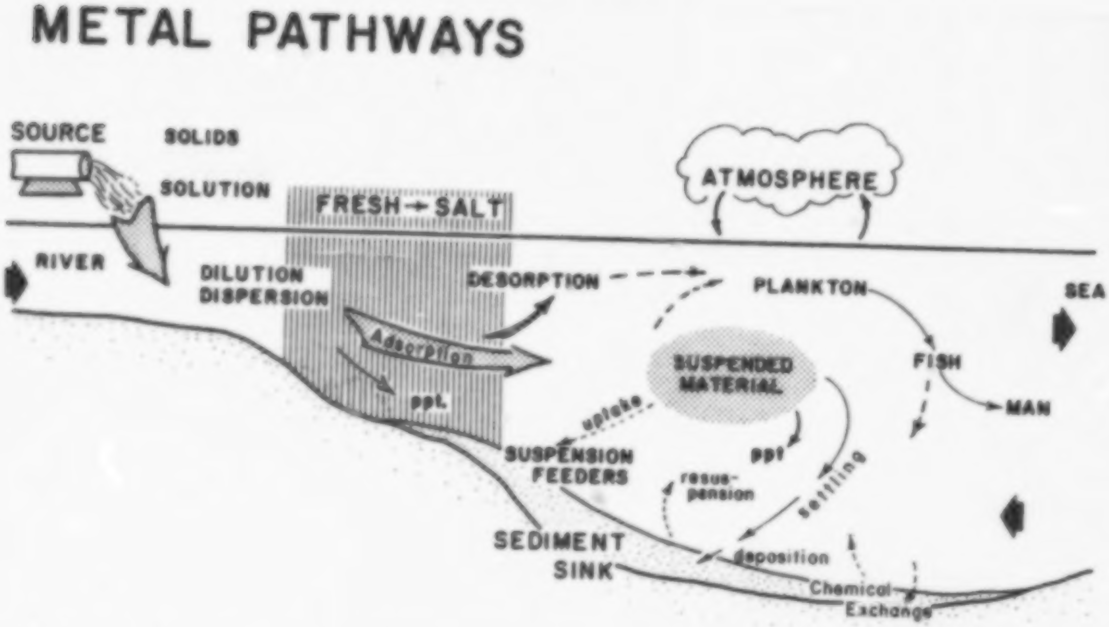

METAL PATHWAYS
SOURCE
SOLIDS
SOLUTION
FRESH → SALT
ATMOSPHERE
RIVER
DILUTION
DISPERSION
DESORPTION
PLANKTON
SEA
Adsorption
ppt.
SUSPENDED MATERIAL
FISH
MAN
uptake
SUSPENSION FEEDERS
ppt
resus-pension
settling
SEDIMENT SINK
deposition
Chemical Exchange

Figure 28. Schematic diagram illustrating the likely pathways of metal cycling in the Bay.

complicated because organisms can extract metals from both dissolved and particulate states, either natural or anthropogenic. Consequently, it is difficult to predict a metal's ultimate destination.

MONITORING STRATEGIES

The purpose of monitoring is to provide a systematic way to detect the input of potentially toxic metals before they build up to hazardous levels. Monitoring should serve as an early warning of danger to man or to a specific resource so that protective actions can be taken. Additionally, monitoring should enhance our quantitative knowledge of the Bay environment, including the ecological balance, as a basis for managing marine resources. The chief questions for toxic metals are: What are the input concentrations and rates? What concentrations accumulate in the sediments relative to natural concentrations? Are these accumulations a function of input rates? At present the quantitative relationship of metal concentrations in sediments to accumulation in particular organisms, communities or resources and their toxicity, is unknown. Until this information is available, it may be possible to rank the metals according to their relative risks or potential hazards following procedures of Hakanson (45) and O'Connor and Stanford (46). Alternately, the monitoring effort can be keyed to meeting some water quality standard yet to be defined. In brief, the initial strategy is to key the monitoring to specific objectives or problems.

To translate the objectives into quantitative terms, it is necessary to measure the concentrations of target metal(s) present in a particular state (dissolved or particulate) and in a particular area(s) of interest that relate to their sources or sinks. Moreover, it is necessary to detect changes in metal loading with time.

Time-series observations are an important approach because toxic inputs are highly variable. They vary with runoff, with sediment influx and with varying discharge of contaminate effluents. As shown in previous sections, metal concentrations of the Bay can vary with the tide, with dispersion or accumulation rates and with seasonal changes in organic loading. Consequently, monitoring should cover a wide range of time scales. These should be sufficient to establish long-term trends, determine norms and differentiate perturbations as well as a gradual build-up.

Monitoring can be organized into source and sink modes. Spatial and temporal design of each mode should be compatible to allow mutual manipulation and interpretation of data. Source areas of the watershed can be monitored effectively from several key stations on or near, the fall line. This is demonstrated by water quality stations occupied by U.S.G.S. (23) at Conowingo, Chain Bridge and Cartersville, which monitored over 75 percent of the watershed area. The data include important metals in several chemical forms, together with important hydrologic data, water quality and suspended sediment concentrations. However, the frequency and number of metal samples is generally limited to less than six per year. They include samples during periods of high inflow and high sediment influx and high metal loading, but they are too sparse to determine the annual mean, minimal values, seasonal trends and response in the Bay. By monitoring point sources of effluent discharges, it may be possible to identify a problem early, or before large amounts of toxics are discharged into the Bay. Monitoring design for point source effluents should follow results of the forthcoming toxic source assessment research. Monitoring of direct discharges, however, may not detect low concentrations of metals that can build up to high levels in the Bay by sedimentary processes or by organisms.

For monitoring sediments, a simple strategy is to sample the upper ¼ cm of fluid mud from sinks or zones of fast deposition. These zones, especially those having clay size sediment, are more sensitive to contamination than other zones and thus provide an early warning of increasing loads from multiple sources. Experience with Kepone contamination (43) showed zones of fast deposition were contaminated first; they also decontaminated first after discharge stopped. Such zones can be located from the history of bathymetric changes and may include deeper parts of tributary mouths, the turbidity maximum, sides of deep basins and dead-end reentrants of shipping channels or anchorages. Freshwater areas near rivers should be avoided because they are subject to flooding and alternate scour and fill. Temporal changes can be revealed by sampling surface fluid mud 2 to 6 times per year depending on deposition rates. Changes in surface sediment can be confirmed by analyzing sediments with depth in cores. A change in concentration as a function of depth implies a change in the rate of cumulative loading, though the sources may not be known. The advantage of this strategy is that it provides maximum data integrated over a time scale of days or months, from relatively few samples. As with any monitoring effort, the replication and representativeness of sampling procedures must be established. Particle size effects should be normalized by analyzing sediment fractions less than 16μ. Because metals associate with one another, as shown in the section "Metal Interactions and Correlations", key metals can be selected and used as surrogates. After samples are analyzed, they should be stored frozen for reference or used as future needs dictate or as instrumentation improves.

RESEARCH NEEDS

The Chesapeake Bay is a very complex estuarine system and our knowledge of hydrodynamic sedimentological and bioecological processes is limited. The knowledge gained in this study can be valuable for predicting some effects of toxic introduction, but it is not sufficient. This study uncovered a number of problems that deserve future research.

1. Since results show maximal concentrations of abnormally high Cd, Cu, Pb and Zn in surface water of the central Bay, a location far from major sources, it remains to determine how they get there. The distribution of metal in various states must be determined together, i.e. dissolved, colloidal, particulate; organic or inorganic; to demonstrate how the metals are partitioned. It remains to learn if metals stimulate production of organic matter like plankton, or by contrast, affect the health of organisms in the central Bay. And, does bio-accumulation and turnover make the metals more, or less, mobile?

2. Metal-organism interactions (suspended) need to be observed seasonally together with nutrients. Furthermore, laboratory experiments utilizing stable and radioisotope tracers are needed to trace changes in metal distributions between water, suspended sediment

and organic material with and without certain bacteria, organic chelators, etc. Additionally, what is the bio-availability of sediment-bound metals?

3. Although the bed is generally assumed to represent a sink for metals and suspended material, this study shows that the bed is dynamic and can also be an important source of suspended material. By repetitive resuspension, metals can be mixed and exchanged with overlying water and suspended material. It remains to discover what metal-sediment interactions take place as resuspension exposes sediment to alternate chemical conditions between the bed and water, e.g. from anoxic to aerobic conditions. What metals are mobilized, or stabilized, by long-continued resuspension? An understanding of these affects is important to evaluating chemical changes induced by dredging.

4. Whereas this study has dealt mainly with metals supplied to the Bay continuously or periodically, episodic events may control their distribution. Floods, hurricanes and storms can produce exceptional conditions for massive resuspension and dispersal of sediment-borne metals. Observations are needed to study the impact of short-term events with respect to: How much sediment and metal is released or mobilized by an event compared to average conditions? What are the corresponding effects on marine resources? What is the sediment and chemical composition of material supplied in different proportions, i.e. river input versus local resuspension? How long does it take to recover, decontaminate or come to a new chemical equilibrium?

5. Since this study reveals that the metal content of Bay suspended material is highly variable, to ascertain the validity of data acquired, future efforts should account for variability in a rigorous statistical sampling plan. In particular, long-term monitoring is needed to distinguish short-term period (tidal) variations and nonperiodic events (storms) from fortnightly, seasonal and yearly changes. Monitoring is needed of source inputs and key points in the Bay at the same time.

6. Much work needs to be done on the transport link between sources of suspended material and toxics in the tributaries and major zones of accumulation in the central Bay. In particular, are the tributaries acting as a source of metals or, by contrast, are they primarily a sink for material supplied from the

Bay via landward flow through the lower layer? It is necessary to establish the source "end-members", or compositional tracers in the Bay and the tributaries, and then to determine their mixing ratios that affect the concentration of particle-associated metals.

7. A basic goal of estuary studies is to develop practical models, either numerical or hydrodynamic, of circulation and sediment transport that can be used for predicting effects of introducing metals, their routes and rates of transport, their discharges at different locations, and effects of river diversions, and varying geometry as channel deepening on transport routes.

SECTION 8

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APPENDIX 1

DATA FOR BLANK CHEMICAL ANALYSIS

	As µg/l	Cd µg/l	Cu µg/l	Fe mg/l	Hg µg/l	Mn mg/l	Ni µg/l	Pb µg/l	Sn µg/l	Zn mg/l
HNO_3 (n=5)	<0.2	<0.2	<1.5	<.014	<0.7	<.001	<1.6	<0.7	<1.3	<.001
HCl (n=5)	<0.7	<0.1	<1.0	<.009	<0.5	<.001	<1.0	<0.7	<1.0	<.001
Distilled, deionized water (n=5)	<0.5	<0.1	<0.8	<.005	<0.5	<.0006	<0.8	<0.8	<0.3	<.001
Run Blanks (50 ml vol., n=20)	<.53	<.29	<1.8	<.56	<.37	<.025	<.83	<2.8	<.83	<.0087
Shipboard filter collection blanks (1 liter vol., n=13)	<.044	<.032	<.090	<.0021	<.022	<.001	<.040	<.14	<.028	<.0038

Metal	Run Blanks (50 ml. vol., n=61)	Shipboard filter collection blanks (1 liter vol., n=17)
As (ug/l)	<.73	<.040
Cd (µg/l)	<.24	<.031
Cu (mg/l)	<.0017	<.0001
Fe (mg/l)	<.40	<.020
Hg (µg/l)	<.40	<.022
Mn (mg/l)	<.023	<.001
Ni (mg/l)	<.002	<.0001
Pb (mg/l)	<.005	<.0002
Sn (µg/l)	<1.0	<.050
Zn (mg/l)	<.009	<.003

APPENDIX 2

RECOVERY OF METALS ADDED TO HNO_3 - DURING DIGESTION

(μg/l concentrations)

Sample	As	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Sn	Zn
A (a)	7.9	1.4	2.2	18	2.2	7.0	7.8	7.7	8.0	6.5
	8.3	1.[illegible]	2.4	19	2.0	7.6	8.2	7.9	8.1	6.6
(b)	8.0	1.4	2.2	18	2.0	7.5	8.3	8.0	8.0	6.8
B (a)	11	2.2	3.3	25	3.0	11	12	12	12	9.4
	12	2.0	3.2	29	3.5	10	12	11	13	9.8
(b)	12	2.1	3.4	27	3.0	11	12	12	12	10
C (a)	17	3.2	5.5	42	5.0	17	20	19	21	17
	18	3.2	5.3	47	5.2	18	21	19	22	17
(b)	20	3.5	5.6	45	5.0	19	21	20	20	17

(a) values obtained (b) known additions

APPENDIX 3

DATA FOR ANALYSIS OF U.S.G.S. STANDARDS AND NATIONAL BUREAU OF STANDARDS BORINE LIVER

USGS STANDARD PCC-1 (n=3)

Metal	Concentration (μg/g)		Standard Values
	$\bar{x}$	s.d.	
Cd	<0.1	-	(.10)
Cu	12	2	11
Fe (%)	6.2	0.1	5.8
Mn	980	30	960
Pb	13	1	13
Zn	32	1	36

USGS STANDARD AGV-1 (n=3)

Metal	Concentration (μg/g)		Standard Values
	$\bar{x}$	s.d.	
Cd	< 0.1	-	(.09)
Cu	54	3	60
Fe (%)	4.4	0.3	4.7
Mn	710	10	730
Pb	32	4	35
Zn	74	3	84

$\bar{x}$ = mean

s.d. = standard deviation

APPENDIX 3, continued

USGS STANDARD G-2 (n=4)

Metal	Concentration (µg/g)		Standard Values*
	$\bar{x}$	s.d.	
As	< 0.2	-	(0.2)
Cd	< 0.1	-	.04
Cu	10.0	0.8	11
Fe (%)	1.8	0.1	1.8
Hg	< 0.2	-	(<0.1)
Mn	210	20	212
Ni	5.5	0.4	5.1
Pb	31	2	31
Zn	85	4	85

USGS STANDARD GSP-1 (n=5)

Metal	Concentration (µg/g)		Standard Values*
	$\bar{x}$	s.d.	
As	< 0.2	-	(0.1)
Cd	< 0.08	-	.06
Cu	30	2	33
Fe (%)	2.5	0.3	2.6
Hg	< 0.2	-	(<0.1)
Mn	221	26	264
Ni	12.6	1.9	12.5
Pb	50	4	51
Zn	98	10	98

*References (5) thru (7)

APPENDIX 3, continued

USGS STANDARD MAG-1 (n=4)

Metal	Concentration (µg/g)		Standard Values*
	$\bar{x}$	s.d.	
Cd	.16	.03	.14
Cu	25.4	0.8	26
Fe (%)	4.3	0.4	4.4
Hg	< 0.4	-	-
Mn	695	35	-
Ni	52	4	51
Pb	22	1	23
Zn	117	5	120

*References (5) thru(7)

USGS STANDARD MAG-1 (n=10)

Metal	Concentration (µg/g)		Standard Values
	$\bar{x}$	s.d.	
Cd	.16	.02	.14
Cu	24	2	26
Fe (%)	4.1	0.3	4.4
Mn	660	40	-
Pb	22	1.5	23
Zn	120	10	120

$\bar{x}$ = mean s.d. = standard deviation

APPENDIX 3, continued

BOVINE LIVER (n=4)

NBS SRM 1577

Metal	Concentration (µg/g)		NBS Values	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.
As	.054	.005	(.055)	-
Cd	.28	.02	.27	.04
Cu	186	9	193	10
Fe	265	15	270	20
Hg	<.033	-	.016	.002
Mn	10.2	.6	10.3	1.0
Ni	2.8	.4	-	-
Pb	.37	.05	.34	.08
Sn	.093	.007	-	-
Zn	128	6	130	10

BOVINE LIVER (n=10)

NBS SRM 1577

Metal	Concentration (µg/g)		NBS Values	
	$\bar{x}$	s.d.	$\bar{x}$	s.d.
As	<.07	-	(.055)	-
Cd	.27	.02	.27	.04
Cu	190	7	193	10
Fe	266	10	270	20
Hg	<.07	-	.016	.002
Mn	10.5	.6	10.3	1.0
Pb	.33	.05	.34	.08
Zn	128	5	130	10

$\bar{x}$ = mean s.d. = standard deviation

APPENDIX 3, continued

USGS STANDARD G-2 (n=10)

Metal	Concentration (µg/g)		Standard Values
	$\bar{x}$	s.d.	
Cd	< 0.1	-	.04
Cu	9.3	1.0	11
Fe (%)	1.7	0.1	1.8
Mn	195	20	212
Pb	30	2	31
Zn	87	5	85

USGS STANDARD GSP-1 (n=8)

Metal	Concentration (µg/g)		Standard Values
	$\bar{x}$	s.d	
Cd	<0.08	-	.06
Cu	29	2	33
Fe (%)	2.4	0.3	2.6
Mn	210	26	264
Pb	50	3	51
Zn	95	8	98

$\bar{x}$ = mean   s.d. = standard deviation

APPENDIX 4

EPA WATER POLLUTION STUDY WP005

Metal	Sample No.	Reported (µg/1)	True Value (µg/1)	Warning Limits (µg/1)
As	1	313	300	163 - 437
	2	25	22	11.3 31.7
Gd	1	67	70	52.0 - 81.0
	2	3.2	2.5	0 - 6.7
Cu	1	384	350	262 - 428
	2	12	11	2.50 - 23.5
Fe	1	938	900	751 - 1054
	2	25	20	0 - 58.1
Hg	1	4.9	8	1.49 12.7
	2	.43	75	.146 - 1.5
Mn	1	521	500	438 - 554
	2	15	15	1.77 - 29.7
Ni	1	323	300	226 - 377
	2	36	30	7.44 - 56.3
Pb	1	404	400	298 - 491
	2	26	24	7.97 - 46.0
Zn	1	438	400	336 - 468
	2	16	16	.665 - 36.6

APPENDIX 5

SUSPENDED SEDIMENT REPLICATE ANALYSES FOR CRUISE 1
(metal/l Bay water filtered)

Station/ Depth (m)	As	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Sn	Zn
	µg/l	µg/l	µg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
17/6	.39	<.04	1.5	1.7	<.05	130	2.7	2.1	0.5	12
	.50	<.14	1.6	2.2	<.10	130	2.2	2.6	0.4	12
	.60	<.14	1.6	2.4	<.10	140	3.6	2.6	0.3	11
	.60	<.14	1.7	2.4	<.10	140	2.2	2.8	0.3	11
$\bar{x}$	.52	<.14	1.6	2.2	<.10	135	2.7	2.5	0.4	12
s.d.	.10	-	C.1	0.3	-	5	0.6	0.3	0.1	0.5
19/0	.18	.10	1.8	1.0	<.07	31	5.9	2.5	0.3	18
	.30	<.14	2.0	.94	<.10	30	6.0	2.4	<0.2	21
	.20	.06	1.9	.84	<.10	28	6.0	1.5	<0.2	20
	.20	.06	2.0	1.1	<.10	40	5.6	1.4	<0.2	19
$\bar{x}$	.22	<.14	1.9	.97	<.10	32	5.9	2.0	<0.3	20
s.d.	.05	-	0.1	.10	-	5	0.2	0.5	-	1
19/5.1	.26	<.05	1.4	1.2	<.06	36	2.4	2.4	<0.2	13
	.30	<.06	1.4	1.8	<.10	44	2.8	1.7	<0.2	12
	.20	<.06	1.4	1.5	<.10	44	3.4	1.9	<0.2	12
$\bar{x}$	.25	<.06	1.4	1.5	<.10	41	2.9	2.0	<0.2	12
s.d.	.05	-	-	0.3	-	4	0.5	0.3	-	0.6
15/9.5	1.4	.069	6.7	6.5	<.08	460	9.4	5.9	0.4	53
	2.0	.078	7.0	7.4	<.10	590	9.3	5.0	<0.2	59
	2.1	<.07	6.7	7.4	<.11	570	10	5.7	<0.3	61
$\bar{x}$	1.8	<.08	6.8	7.1	<.11	540	9.6	5.5	<0.4	57
s.d.	0.4	-	0.2	0.5	-	70	0.4	0.4	-	4

APPENDIX 5

SUSPENDED SEDIMENT REPLICATE ANALYSES FOR CRUISE 2
(dry weight)

Station	As	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Sn	Zn
	µg/g	µg/g	µg/g	%	µg/g	mg/g	µg/g	µg/g	µg/g	mg/g
3	3.3	0.05	2.7	1.2	< .06	.25	12	8.3	.54	.053
	3.3	0.04	3.0	1.2	< .06	.26	10	9.2	.47	.051
	3.6	0.03	2.6	1.3	< .08	.26	8.3	9.1	.62	.052
$\bar{x}$	3.4	0.04	2.8	1.2	< .08	.26	10	8.9	.54	.052
s.d.	0.2	0.01	0.2	.06	-	.01	1.8	0.5	.07	.001
13	6.0	.25	35	4.3	< .06	3.3	73	62	1.9	.26
	6.2	.23	31	3.9	0.2	2.9	61	61	2.1	.25
	5.6	.18	27	3.6	< .06	2.8	54	54	1.8	.22
$\bar{x}$	5.9	.22	31	3.9	<0.2	3.0	63	59	1.9	.24
s.d.	0.3	.03	4	0.3	-	0.2	9	4	0.2	.02
20	5.3	.05	34	2.1	< .06	1.5	19	45	1.9	.13
	4.8	.09	33	2.0	< .03	1.5	22	41	1.7	.13
	4.2	.09	34	2.1	< .02	1.5	25	36	2.0	.15
$\bar{x}$	4.8	.08	34	2.1	< .06	1.5	22	41	1.9	.14
s.d.	0.5	.02	0.6	.06	-	-	3	4	0.2	.01

$\bar{x}$ = mean

s.d. = standard deviation

APPENDIX 5, continued

SUSPENDED SEDIMENT REPLICATE ANALYSES FOR CRUISE 2
(metal/1 Bay water filtered, n=3)

Station/ Depth (m)	As µg/1	Cd µg/1	Cu µg/1	Fe mg/1	Hg µg/1	Mn µg/1	Ni µg/1	Pb µg/1	Sn µg/1	Zn µg/1
4/7.3										
$\bar{x}$	.31	.071	1.5	.93	.23	23	2.2	1.3	<.29	15
s.d.	.05	.010	0.2	.16	.02	4	1.1	0.1	-	1
6/11										
$\bar{x}$	5.0	.24	8.5	14	.56	160	13	3.0	<.88	67
s.d.	0.7	.06	1.3	1	.12	4	2	0.4	-	11
14/10										
$\bar{x}$	1.1	.043	4.3	3.8	<.060	270	5.7	6.1	.33	35
s.d	0.1	.008	0.5	0.5	-	20	0.6	0.6	.11	6

$\bar{x}$ = mean

s.d.= standard deviation

Cruise 4

Suspended Sediment Replicate Analyses

(Metal /1 Bay water filtered, n=3)

Station/ Depth (m)	As µg/1	Cd µg/1	Cu µg/1	Fe mg/1	Hg µg/1	Mn µg/1	Ni µg/1	Pb µg/1	Sn µg/1	Zn µg/1
3/0										
$\bar{x}$	<.12	.26	.42	.20	<.041	11	.12	1.2	<.20	5.0
s.d.	-	.08	.05	.01	-	1	.01	0.1	-	0.7
5/8										
$\bar{x}$	<.16	<.20	2.1	.16	<.050	7.3	<.18	.75	<.30	11
s.d.	-	-	0.8	.01	-	1.0	-	.06	-	3
11/0										
$\bar{x}$	<.12	.15	.94	.043	<.047	14	<.30	.80	<.19	6.2
s.d.	-	.05	.23	.002	-	2	-	.18	-	1.9
24/16										
$\bar{x}$	.17	<.081	1.2	.54	<.051	100	.58	1.5	.12	6.6
s.d.	.03	-	0.1	.01	-	6	.16	0.2	.01	1.1

$\bar{x}$ = mean

s.d. = standard deviation

APPENDIX 5, continued

SUSPENDED SEDIMENT REPLICATE ANALYSES FOR CRUISES 5 AND 6 APRIL-MAY, 1980 (metal/l Bay water filtered)

Station/ Depth (m)	Time	Cd µg/l	Cu µg/l	Fe mg/l	Mn µg/l	Pb µg/l	Zn µg/l
19/6.2	1200						
x̄(n=4)		.071	1.8	1.5	110	4.3	11
s.d.		.016	0.2	0.1	5	0.3	1
17/9.8	1000						
x̄ (n=3)		<.032	3.7	2.8	200	3.8	18
s.d.		-	0.2	0.1	15	0.1	1
15/6.4	1000						
x̄ (n=3)		<.021	.98	.82	58	2.0	7.4
s.d.		-	.04	.02	1	0.1	1.0
11/0	1600						
x̄ (n=3)		.050	1.0	.19	21	2.6	9.1
s.d.		.010	.05	-	1	0.4	1.7
13/13.1	-						
x̄ (n=4)		.33	4.4	1.7	180	4.9	14
s.d.		.07	0.7	0.2	20	0.5	2

APPENDIX 5

SURFACE FLUID MUD REPLICATES FOR CRUISES 3 AND 4 (dry weight, n=3)

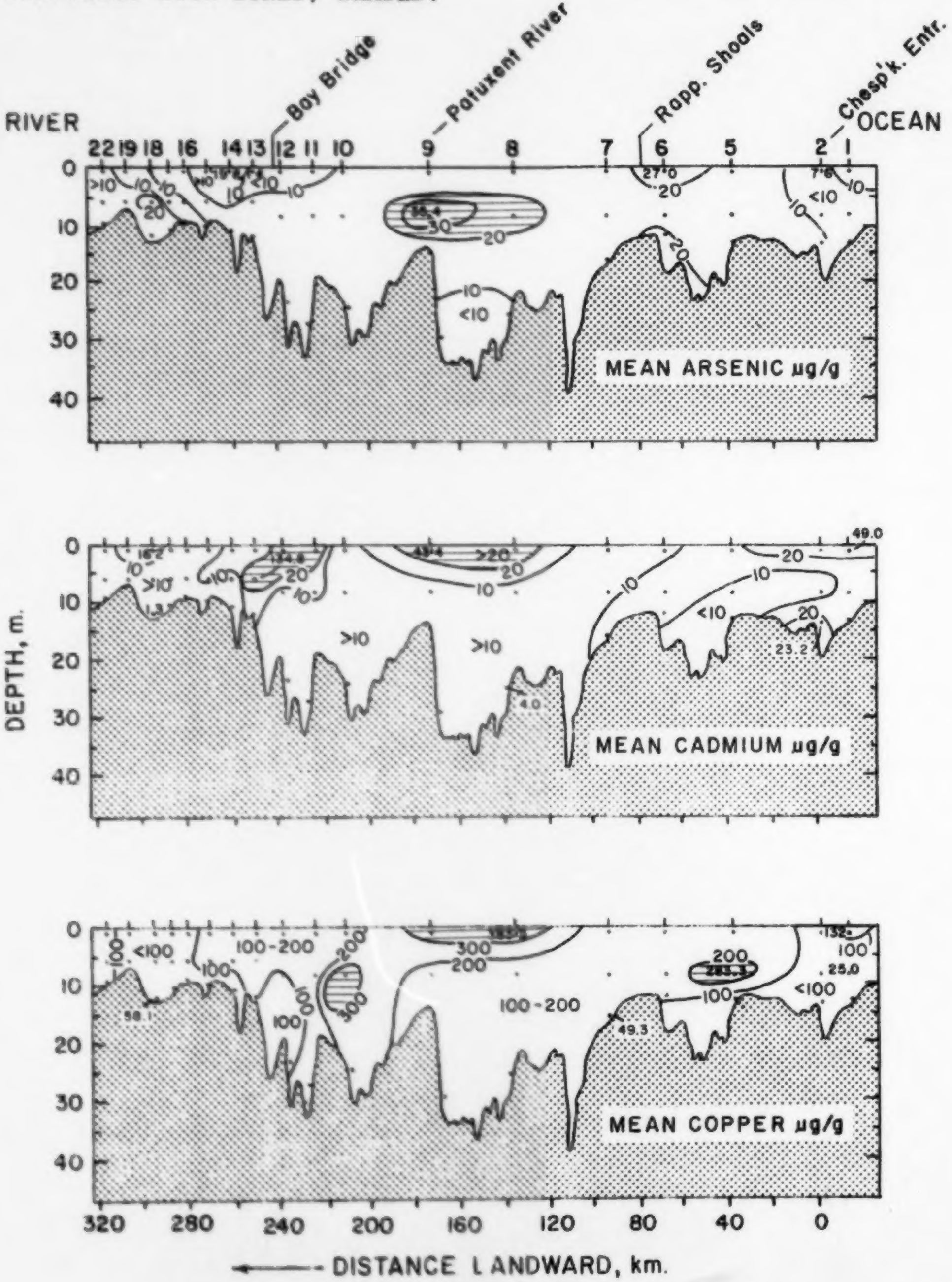
Station (Cruise)	As µg/g	Cd µg/g	Cu µg/g	Fe %	Hg µg/g	Mn mg/g	Ni µg/g	Pb µg/g	Sn µg/g	Zn mg/g
19 (3)										
x̄	1.4	.42	36	2.9	<.094	1.9	44	40	<.22	.23
s.d.	0.1	.05	3	0.1	-	0.1	3	4	-	.02
20 (3)										
x̄	2.2	.29	35	3.3	<.095	1.9	21	79	<.22	.32
s.d.	0.1	.03	5	0.1	-	0.1	3	7	-	.01
1 (4)										
x̄	.89	<.064	.45	.78	<.096	.17	3.0	3.1	<.22	.020
s.d	.09	-	.04	.04	-	.01	0.2	0.3	-	.001
6 (4)										
x̄	2.3	.057	5.9	1.5	<.078	.18	11	7.9	<.20	.043
s.d	0.2	.005	0.7	0.1	-	.01	1	0.7	-	.003
17 (4)										
x̄	1.1	.51	35	2.8	<.089	1.4	43	34	.45	.17
s.d	0.1	.01	2	0.1	-	0.1	2	2	.04	.01

x̄ = mean

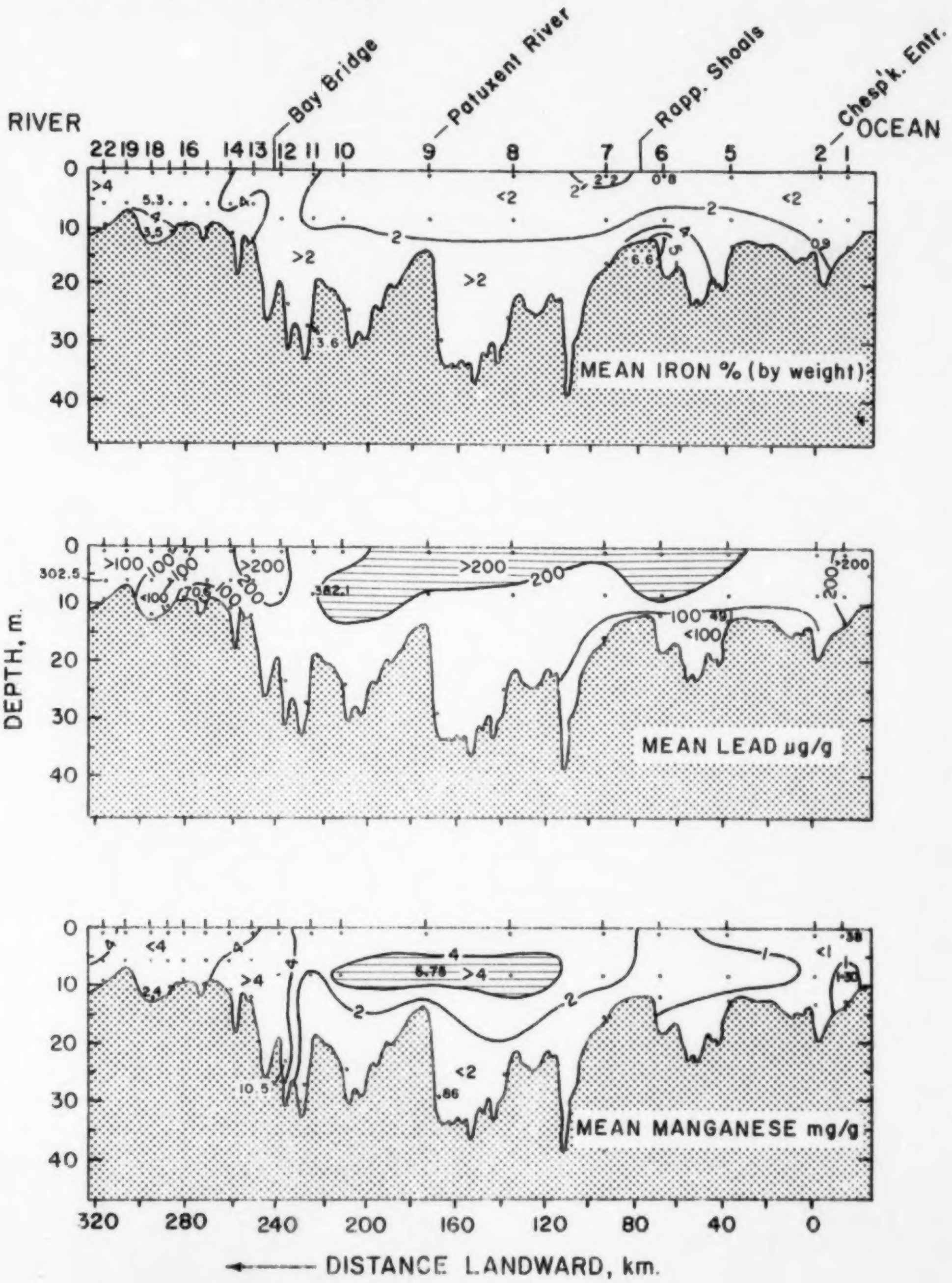
s.d. = standard deviation

APPENDIX 6

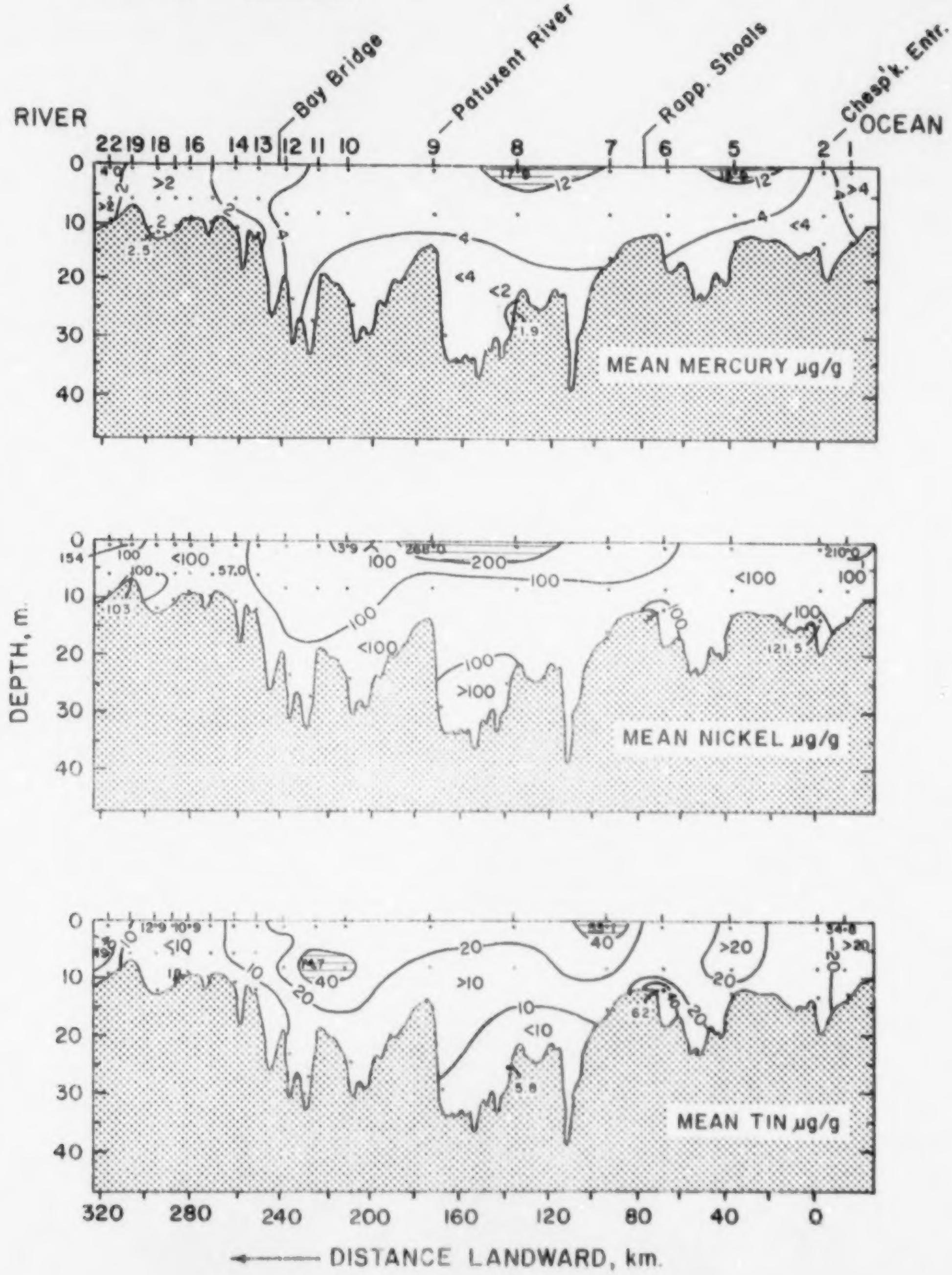
LONGITUDINAL-DEPTH DISTRIBUTIONS OF MEAN METAL CONCENTRATION IN SUSPENDED MATERIAL, WEIGHT PER WEIGHT, FOR ALL AVAILABLE OBSERVATIONS OF THIS PROJECT ALONG THE AXIS OF CHESAPEAKE BAY. ANOMALOUS HIGH ZONES, SHADED.



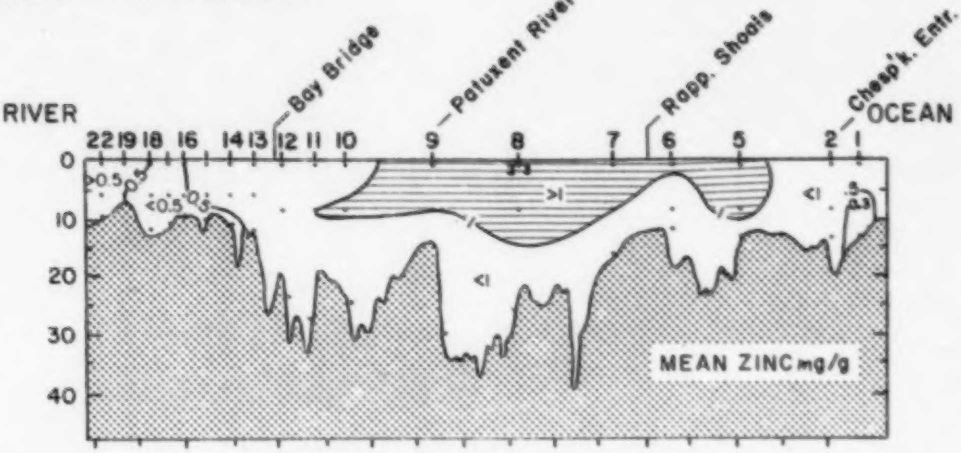
APPENDIX 6, continued



APPENDIX 6, continued

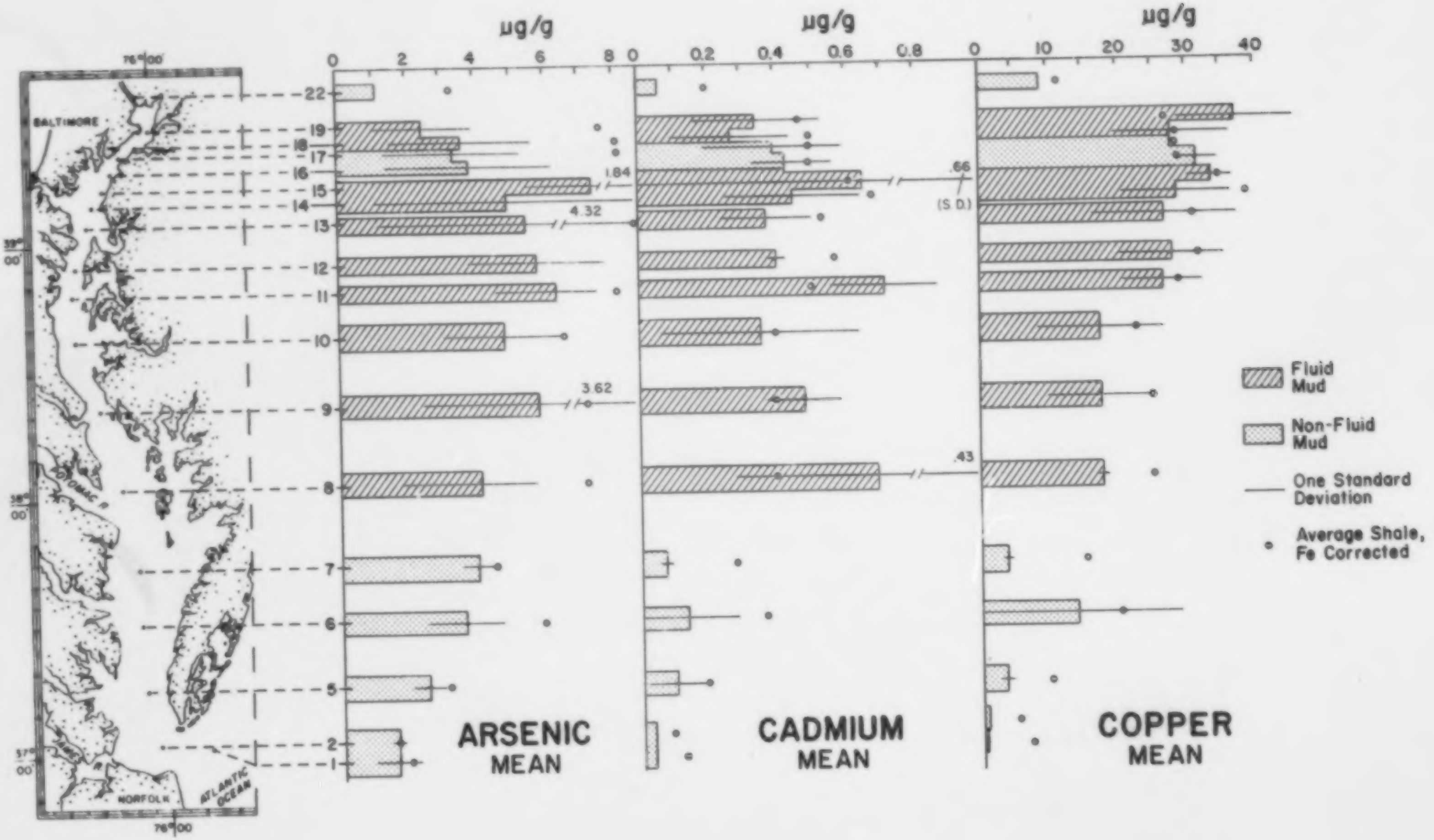


APPENDIX 6, continued

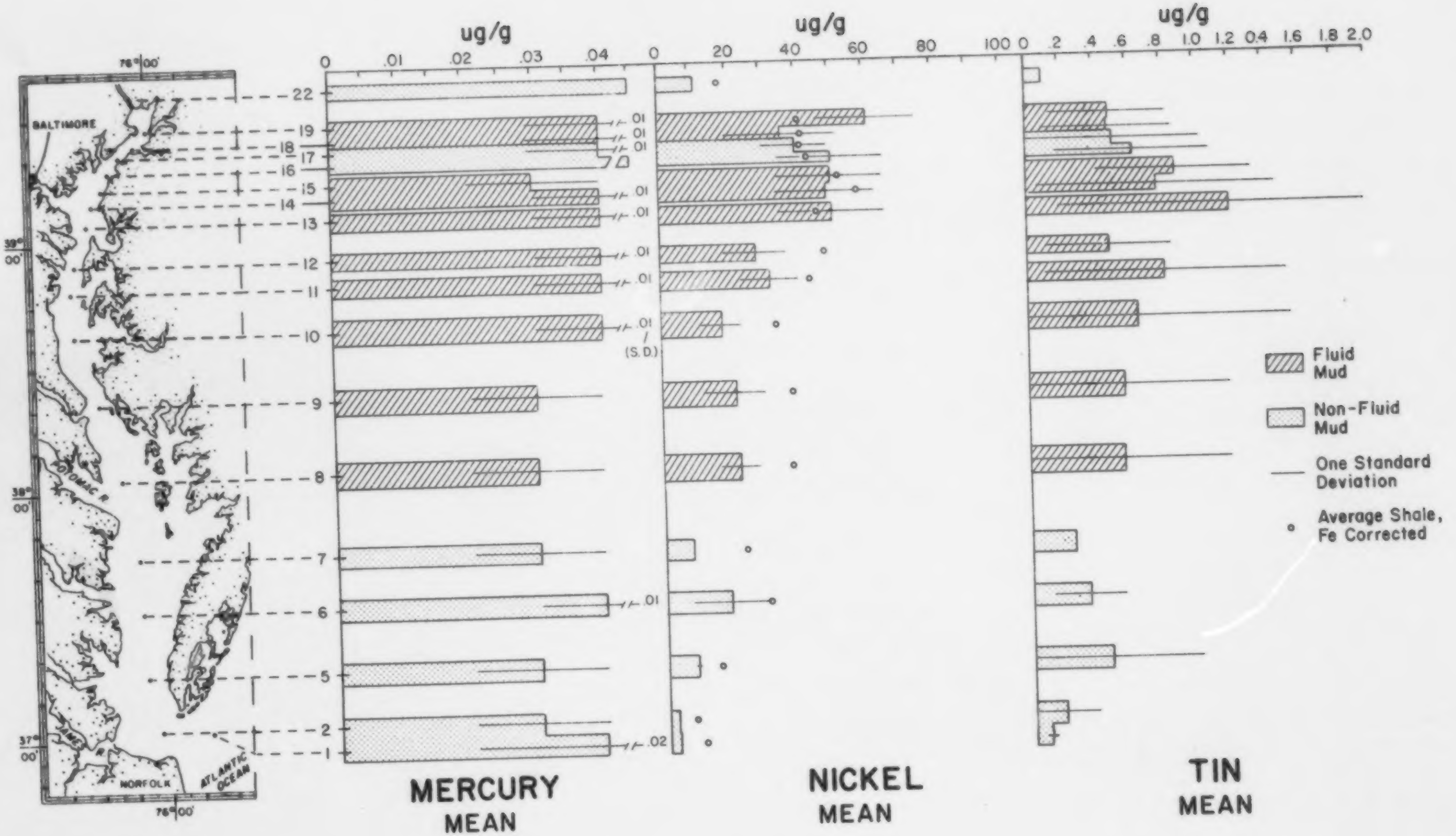


APPENDIX 7

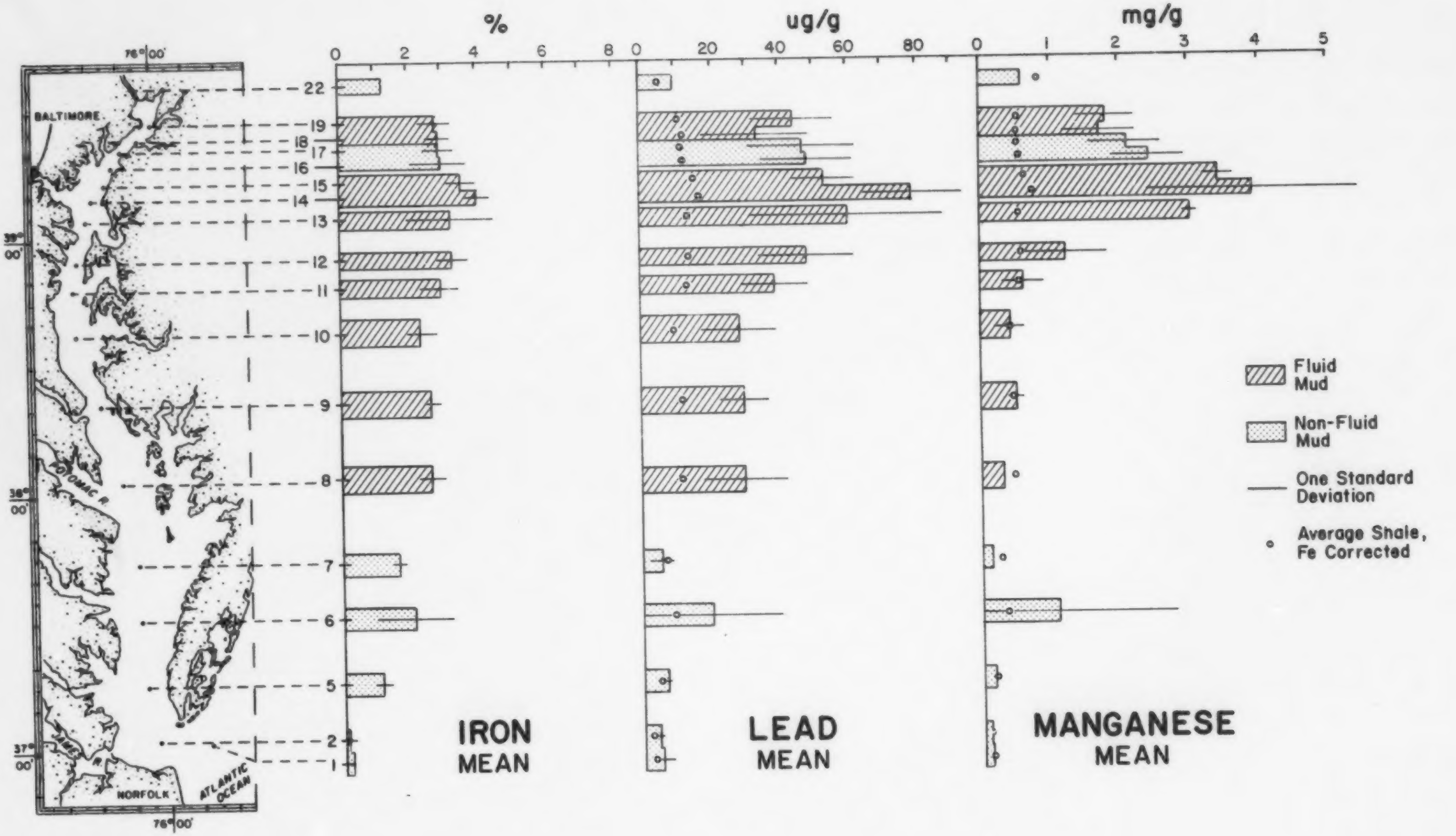
LONGITUDINAL DISTRIBUTIONS OF MEAN METAL CONCENTRATION IN FLUID MUD AND BED SEDIMENT FOR ALL AVAILABLE SAMPLES FROM THIS PROJECT ALONG THE AXIS OF CHESAPEAKE BAY.



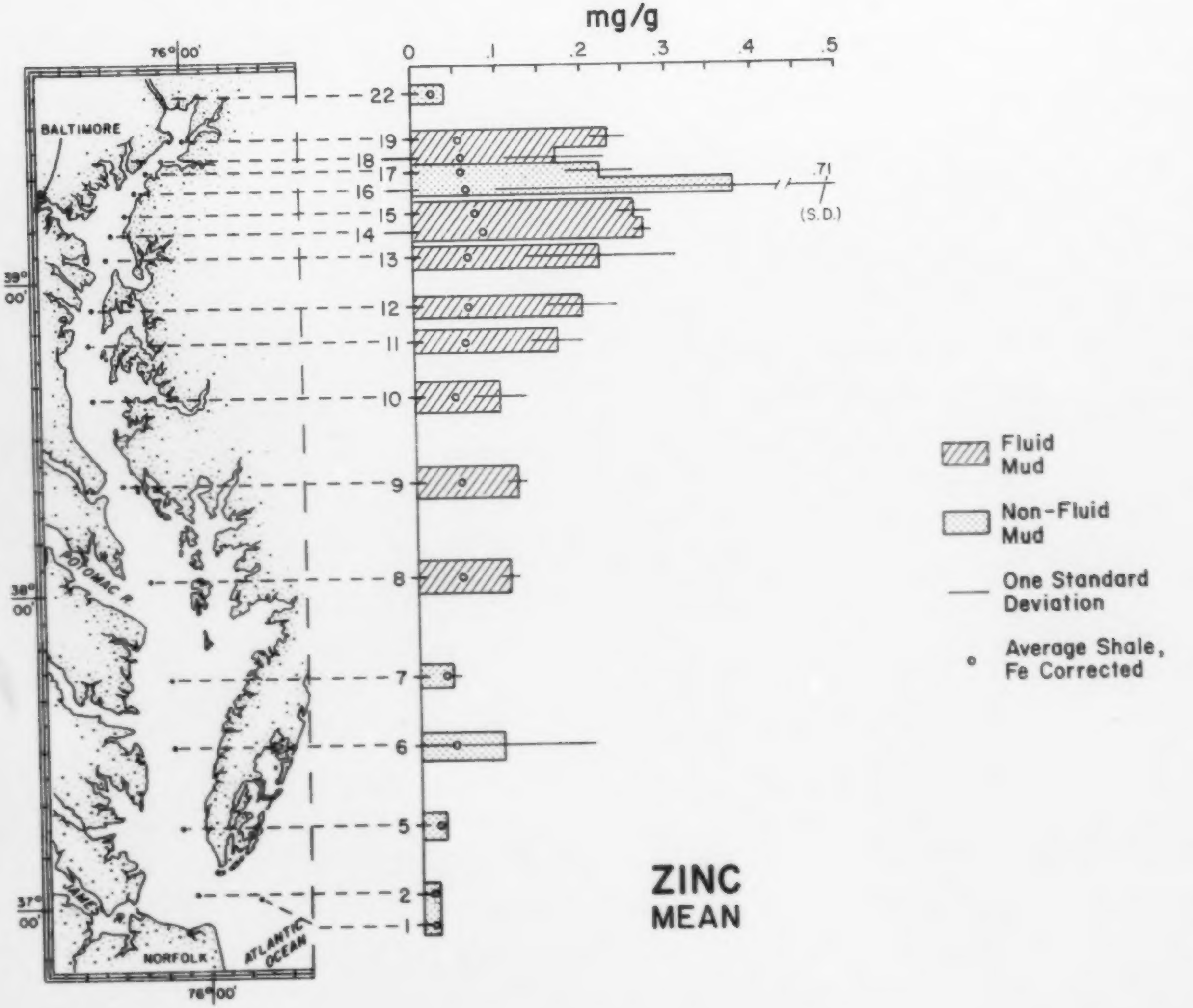
APPENDIX 7, continued



APPENDIX 7, continued



APPENDIX 7, continued

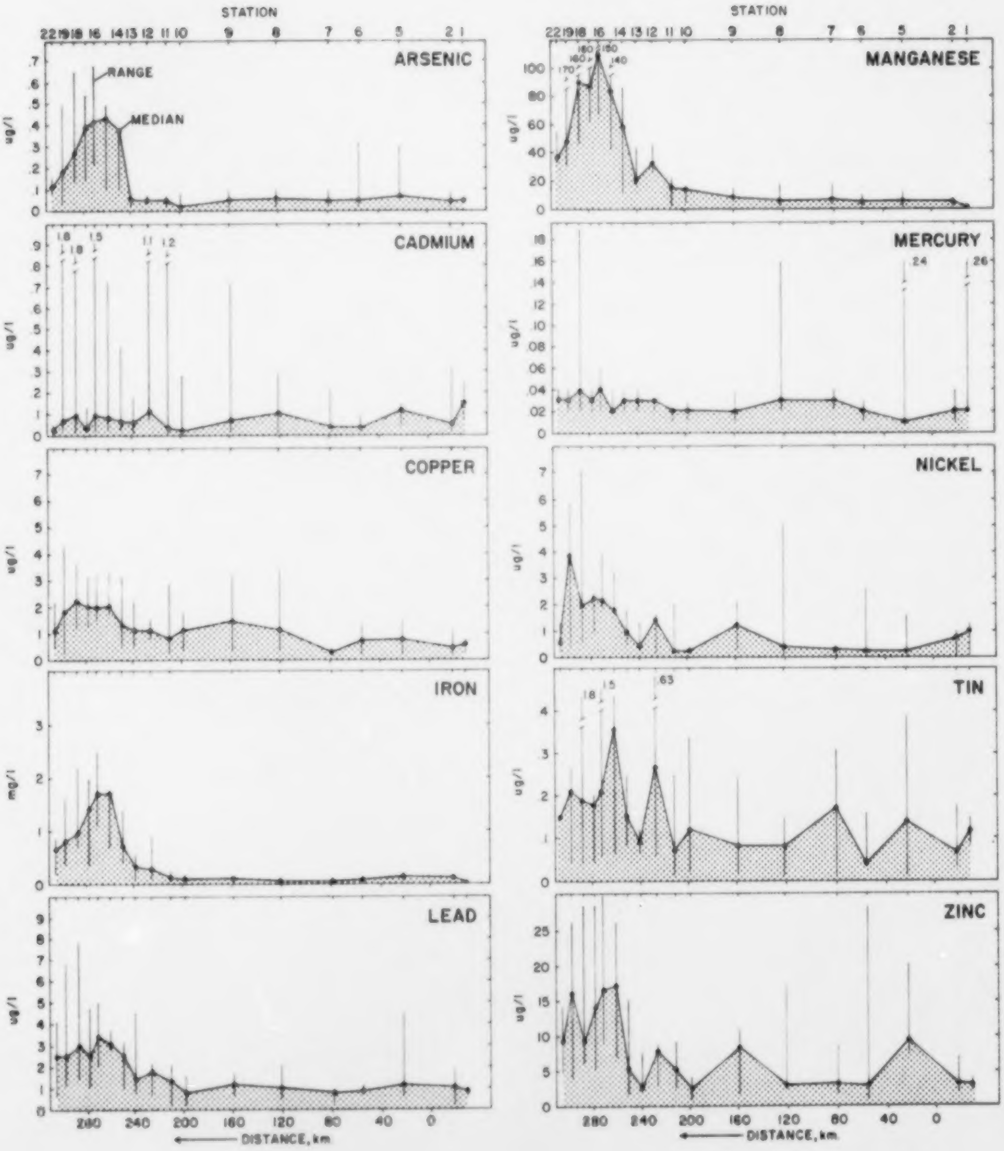


APPENDIX 8

DISTRIBUTION OF METAL CONTENT, WEIGHT PER VOLUME, IN SURFACE AND NEAR-BOTTOM SUSPENDED MATERIAL WITH DISTANCE ALONG THE BAY AXIS. MEDIAN VALUES AND RANGE OF CONCENTRATIONS FROM ALL AVAILABLE OBSERVATIONS OF THIS PROJECT.

METALS IN SUSPENDED MATERIAL

SURFACE



APPENDIX 8, continued

METALS IN SUSPENDED MATERIAL

NEAR-BOTTOM